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Investigation of Asphalt Pavement Mixture Blending Utilizing Analytical Chemistry Techniques

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Investigation of Asphalt Pavement Mixture Blending Utilizing Analytical Chemistry Techniques

A Dissertation Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Benjamin Frank Bowers
December 2013

DEDICATION

This work is dedicated to my lovely wife, Jessica Bowers, and my wonderful family.
Thank you for all of your love and support.

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ABSTRACT

The use of Reclaimed Asphalt Pavement (RAP) in new pavement mixtures is a topic of interest throughout the transportation industry and academia due its economic and environmental implications. There is concern however about how well the binder from the RAP blends with new, virgin binder when the mixture is created. Insufficient blending of the aged and unaged binders may compromise the long-term pavement performance. In this study, an enhanced staged extraction method is coupled with two chemical testing techniques to develop a novel approach for evaluating blending efficiency from a qualitative and quantitative perspective: Gel Permeation Chromatography (GPC) and Fourier Transform Infrared Spectroscopy (FTIR). Both chemical testing techniques can be used to study asphalt binder aging.

The staged extraction method consists of washing an asphalt mixture with solvent to remove layers of asphalt binder from the binder film. The study presented in Chapter 2 uses FTIR and fractionation to investigate whether sequential dissolution of the binder fractions occurs rather than a true removal of layers. Sequential dissolution is found to occur with some common asphalt solvents that were tested, and trichloroethylene (TCE) is determined to be the best solvent for staged extraction.

In Chapter 3 an approach using GPC and FTIR is used to analyze binder recovered by staged extraction to evaluate the blending efficiency of RAP and virgin binder. Partial

blending of the binder is found to occur throughout the binder film. Chapter 4 explores the impact of mixing time, mixing temperature, and the addition of Warm Mix Asphalt (WMA) additives on blending efficiency using rheological testing and GPC. All mixing factors were found to impact the asphalt mixture. Blending efficiency, estimated with a blending ratio, was less than 80% in all cases.

The staged extraction method is employed with FTIR in Chapter 6 to determine the most efficient way to create a laboratory-aged artificial RAP for controlled experiments. In Chapter 7 GPC was used to develop a new method of determining whether fine aggregate used in pavement mixtures is contaminated with asphalt binder, which could potentially blend with the virgin binder and compromise the pavement performance.

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CHAPTER I

RESEARCH BACKGROUND, OBJECTIVES, AND LITERARY OVERVIEW

1.1 Research Background

The National Asphalt Pavement Association (NAPA) reports that over 94% of the United States' pavements are flexible asphalt pavements. Additionally, asphalt pavements are known to be America's most recycled material (NAPA 2013). Asphalt binder, a byproduct of the crude oil refining process, is a recyclable material that can be reused without down cycling. Two major sources of recycled binder are from reclaimed asphalt pavements (RAP) as well as from recycled asphalt shingles (RAS).

The asphalt cement in pavement tends to oxidize or "age" over time, which results in a stiffening of the binder. The aging process is indicative of chemical changes within the bitumen. These chemical changes can be characterized using different analytical chemistry techniques such as Gel Permeation Chromatography (GPC) and Fourier Transform Infrared Spectroscopy (FTIR). Furthermore, a great deal of research has been conducted that helps identify the chemical changes as they relate to the mechanical properties of the asphalt binder and its effect on the resulting pavement mixture performance.

There is looming concern over how efficiently the aged recycled asphalt binder blends with virgin, neat asphalt binder during the pavement mixing process. It is imperative that researchers and practitioners understand the efficiency with which reclaimed binder blends with virgin binder. Without an understanding of blending efficiency it is very difficult to predict the long-term performance of the pavement, thus making high-RAP

pavements (>40% RAP) hard to legitimately construct with an estimated pavement life of 10-15 years.

Additionally, there are concerns over multiple issues in asphalt paving which may be solved through the application of different analytical chemistry testing techniques. Considerable question has been made of whether common asphalt solvents such as trichloroethylene (TCE), tetrahydrofuran (THF), and toluene sequentially dissolve asphalt binder fractions. While there is no concern over whether or not the solvent will eventually dissolve all of the binder, questions do arise when simply washing the binder or pavement mixture successive times with the solvent. There is also often a need, in studying RAP blending efficiency, to create a laboratory aged or "artificial" RAP pavement. Many methods have been applied to create such a RAP, but one must question how effectively the binder is aged and how realistic the resulting RAP is compared to a true field-collected RAP.

1.2 Research Objectives and Significance

The research objectives presented below and in Figure 1.1 are addressed herein:

1. Chapter 2: Validate the staged extraction method for applicability to blending efficiency.

2. Chapter 2: Investigate mechanism of asphalt cement solubility in three common asphalt solvents, trichloroethylene (TCE), tetrahydrofuran (THF), and toluene, and study the possibility of sequential dissolution of binder fractions using FTIR.
3. Chapter 3: Apply the findings of the staged extraction method to investigate laboratory prepared RAP pavement mixtures for blending efficiency using GPC and FTIR.
4. Chapter 4: Investigate blending efficiency of virgin and RAP binder under varying mixing scenarios to study the effects of temperature, mixing time, and the addition of warm mix asphalt additives.
5. Chapter 5 and Chapter 6: Create a new and innovative method for determining whether fines used for asphalt pavement are contaminated with naturally occurring asphalt. Develop procedure for creating artificial RAP for controlled laboratory experiments.

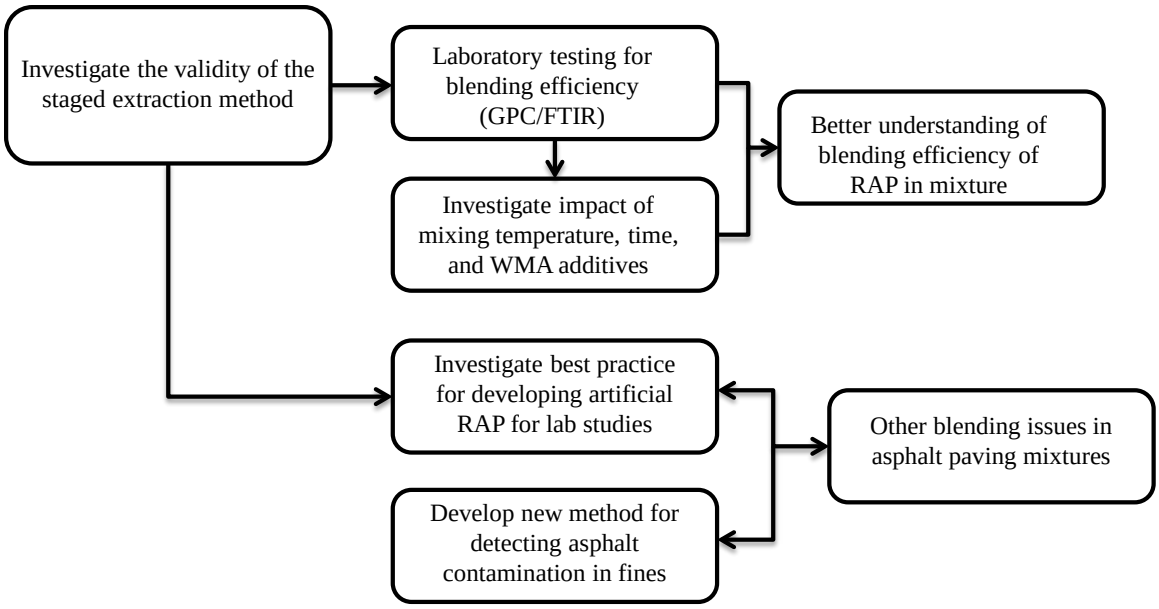

Figure 1.1 Flow chart of research plan

Completion of these research objectives sheds new light on the blending efficiency of virgin binder and reclaimed binders helping in the efforts to better predict the pavement performance of recycled mixes. Furthermore, the methods used may be able to be used for additional studies of different reclaimed materials such as Recycled Asphalt Shingles (RAS).

Further development of chemical testing methods as applied to the asphalt industry will mark progress in the advancement of interdisciplinary studies which apply molecular and nano-scale technologies to the study of infrastructure materials. These innovative approaches to solving the problems of contamination and selective solubility characteristics will allow for more confident research within the asphalt research

community, ultimately yielding knowledge that is highly applicable to the design, construction, and lifetime of the pavement.

1.3 Arrangement of Dissertation

This dissertation is divided into seven chapters. Chapter one provides background and literature support for the studies presented herein. Chapters two through six are journal articles that have either been published, in press, tentatively accepted, or are in review at the time of the composition of this dissertation. Chapter two investigates the potential for common asphalt solvents, trichloroethylene (TCE), toluene, tetrahydrofuran (THF), and decahydronaphthalene (decalin) to sequentially dissolve fractions of asphalt binder when using staged extraction (Objectives 1 and 2). Chapter three applies staged extraction to an asphalt mixture that contains both RAP and virgin materials to investigate the blending efficiency by means of the chemical testing techniques Gel Permeation Chromatography (GPC) and Fourier Transform Infrared Spectroscopy (FTIR) (Objective 3). The study presented in chapter four investigates the effects of mixing conditions such as temperature, mixing time, and the influence of Warm Mix Asphalt (WMA) additives on the blending efficiency of asphalt mixtures containing RAP (Objective 4). Chapter five explores possible solutions to the development of a laboratory aged, artificial RAP for controlled laboratory experiments (Objective 5). The research presented in chapter six is an innovative new method utilizing gel permeation chromatography to identify the presence of asphalt contamination within the fine aggregates that are intended to be used

for a new paving mixture (Objective 5). The final chapter, chapter seven, presents an outline of the conclusions from all five studies as well as recommendations for future research in this area.

1.4 Literary Overview

1.4.1 Blending Efficiency of Reclaimed Asphalt Pavement

A major cause of concern in the reuse of asphalt binder from a reclaimed asphalt source such as RAP or RAS is whether or not the reclaimed binder truly blends with the virgin binder. “Black rock” theory is based on the premise that the RAP may actually perform as nothing more than an aggregate. While this may provide some use of the RAP as a recycled aggregate, the major economic savings come from the reuse of the RAP binder. However, if the stiff, oxidized binder does not truly blend with the virgin binder in the mixture, the use of blending charts commonly used in pavements where RAP is included is unnecessary (Huang et al. 2005a, McDaniel et al. 2000). Figure 1.2 shows three of the different possible outcomes from combining RAP and virgin binder.

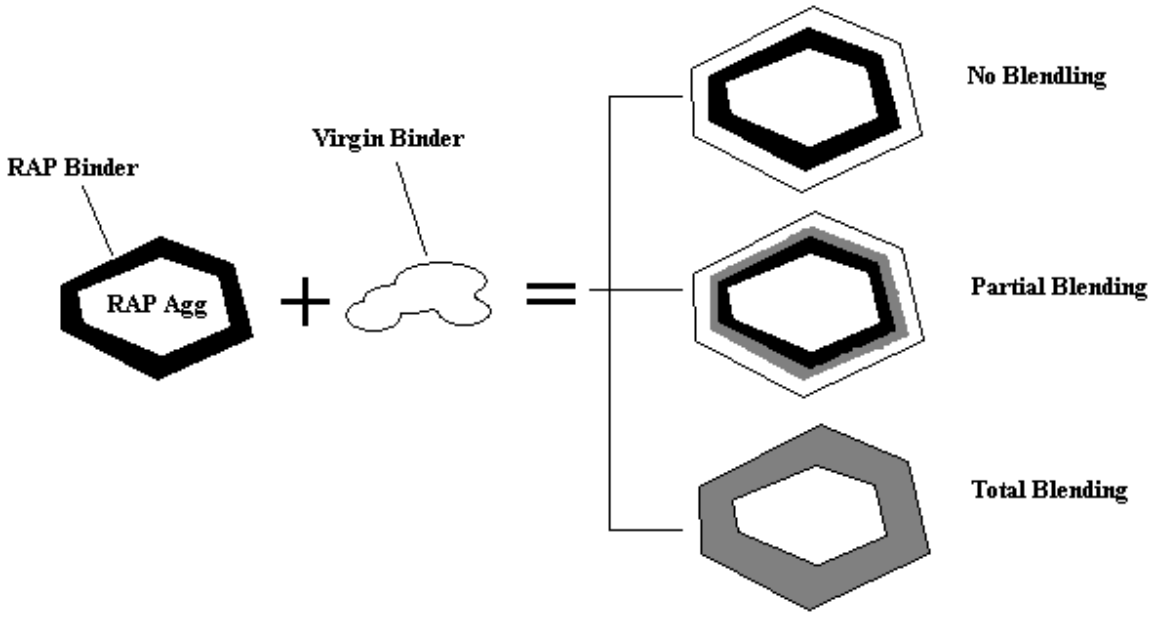

Figure 1.2 Three possible outcomes of blending RAP with virgin binder

Blending charts are commonly used in practice as a guide to safe addition of RAP. The premise of these charts is that up to a certain percentage of RAP can be added without needing to decrease or "bump" the binder performance grade in order to counteract the stiff, oxidized RAP binder (Khandal and Foo 1997). Common practice is to add up to 15% RAP without changing binder grade and between 15-25% RAP by only reducing one binder grade with respect to both high and low temperatures. Beyond 25% RAP a blending chart is required to estimate the binder grade necessary to create a mixture that will perform to SuperPave standards. The use of blending charts in current practice was further supported by NCHRP 9-12 conducted by McDaniel et al. (2000) which concluded that partial blending does occur to a significant extent. In order to further refute the "black rock" theory, Soleymani et al (2000) simulated a "black rock" condition. The researchers created three mixtures, denoted Case A, Case B, and Case C. The black rock

scenario, Case A, was created by extracting the binder from a RAP and adding only the recovered aggregate to a new mixture of virgin aggregate and virgin binder. Case B is considered a "true" mixture, where the RAP is added directly to the mixture with the virgin aggregate and virgin binder. The "total blend", Case C, was created by mechanically blending the virgin binder and recovered RAP binder and adding it to the virgin and RAP aggregate to make the mixture. All three cases were evaluated using the SuperPave Shear Tester (SST) with frequency sweep, simple shear, and repeated sheer at a constant height testing scenarios. The researchers compared the results of the three cases statistically and found that at a 10% RAP content none of the cases were differentiable. However, at 40% RAP content, 45% of the "true" RAP mixtures (Case B) performed similarly to the 100% blend (Case C), while only 5% performed similarly to the "black rock" scenario (Case A). The remaining 50% of the mixtures did not perform similarly to either Case A or Case C. This study concluded that RAP does not behave as a black rock considering at a high RAP content (40%) the mixture performed similarly to that of a 100% blend. The researchers also conclude that at least partial blending occurs in almost all cases. Additionally, an important conclusion is that the suggestion that up to 15% RAP can be added without a need to resort to blending charts is reasonable on the basis of this study.

Other attempts to address the blending efficiency question have been made. McDaniel et al. (2012) address this issue by using the "Bonaquist Approach" (Bonaquist 2007) which considers pavement volumetrics and their relationship to the dynamic modulus (E*) of

the mixture. The Hirsch Model is used to create an estimated E* master curve. Twenty-four mixtures were considered utilizing multiple contractors. Mixtures were created mixes using a virgin Performance Grade (PG) 64-22 asphalt binder with 0%, 15%, 25%, and 40% RAP contents. Additionally, a softer PG58-28 virgin binder was used at 25% and 40% RAP content. Each of the contractors made efforts to keep the mixture gradation as close as possible to their counterparts. The binder was recovered using *n*-propyl bromide and the complex modulus (G*) was investigated using the Dynamic Shear Rheometer (DSR) and low temperature performance was tested using the Bending Beam Rheometer (BBR). These values were used in the Hirsch Model to estimate the E* master curve on the assumption that the recovered asphalt could be considered a 100% blend between the virgin binder and RAP binder. The E* master curve was then generated in the lab through performance testing for each of the mixtures. If the estimated E* matched the mixtures true E*, the mixtures were considered to be 100% blended. Out of 21 samples containing RAP only three were considered to have poor blending and one had partial blending.

A similar study was conducted by Mogawer et al. (2012) looking specifically at 9.5 mm and 12.5 mm SuperPave mixtures. These mixtures comprised of PG58-22 binder containing 30% and 40% RAP, PG64-22 binder containing 0%, 20%, 30%, and 40% RAP, and PG52-34 and PG64-28 binder mixtures containing 0%, 20%, 30%, and 40% RAP. Samples were collected from New Hampshire, Vermont, and New York. The Christenson-Anderson model was used to develop a master curve for the extracted and

recovered binders from each mixture. These estimated master curve was then compared to the E* master curve of the mixture to determine the degree of blending. A conclusion of this study focused on the handling, mixing, and storage of the material in terms of its impact on the mixture stiffness and cracking properties. The authors state that blending efficiency seemed to be impacted by the discharge temperature of the mixture from the silo.

1.4.2 Staged Extraction

With the credible and commonly accepted support of NCHRP 9-12 it is concluded that *partial* blending does occur between virgin and RAP binder. However, the question remains of how much blending does this equate to? In attempt to address this problem, Huang et al. (2005a) used the staged extraction method to evaluate "layers" of binder. The following Figure 1.3 outlines the concept proposed by the researchers. RAP had been mixed with virgin aggregate and binder and then removed from the mixture. The RAP, which has now come in contact with virgin binder, was dipped into four successive beakers of fresh trichloroethylene (TCE), a common asphalt solvent, for 3 minutes per wash. Each wash removed a "layer" of asphalt binder from the aggregate. These layers were then recovered and evaluated using the dynamic shear rheometer (DSR) and Finite Element Analysis. The researchers concluded that upon blending a composite layer of binder does form around the RAP particle; however there is actually stiffening in the layer closest to the aggregate.

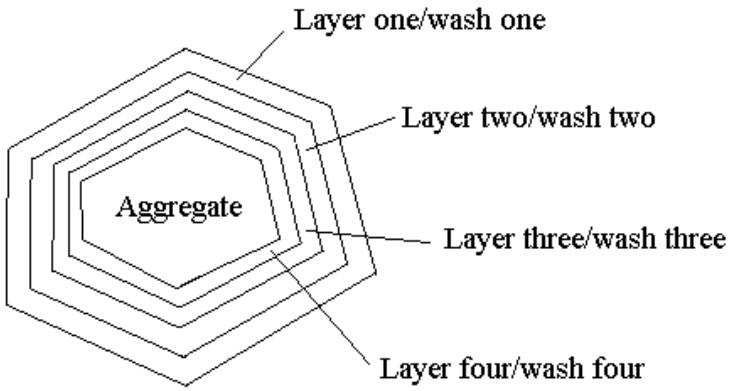

Figure 1.3 Layered system in Staged Extraction Method, inspired by Huang et al. 2005a

In 1979 a similar study was conducted by the Iowa Department of Transportation. Six samples, some of which contained RAP, were taken from asphalt pavements. The binder was recovered after two washes with TCE. The binders were then subjected to penetration testing and in most cases the penetration values were identical. However, some testing indicated that the innermost layer was softer than the outer layer. This was attributed to the presence of shale within the aggregate which has a tendency to selectively absorb the lighter fractions of the asphalt binder. Additionally, a laboratory study was conducted where a penetration 60 asphalt was used to coat an aggregate, which was then age hardened in an oven. After age hardening, the mixture was painted with 200 penetration asphalt and washed three successive times, yielding three layers. All layers were tested and yielded values well below a 200 penetration, meaning that the binder was in fact blending to some degree. (Zearley 1979)

In 1980 Carpenter and Wolosick investigated the use of rejuvenators in RAP material. This research entailed the use of staged extraction in two layers, similar to that of

Zearley's work in 1979. However, the researchers also increased mixing time to investigate its effect on the ability for the rejuvenating agent to penetrate the RAP binder. While it was concluded that the two extracted layers did have different performance characteristics as indicated by penetration testing, it was found that as the mixing time increased the two layers penetration values moved closer together. The movement of the penetration values closer together is indicative of binder uniformity occurring due to the penetration of the rejuvenator within the recycled binder.

Noureldin and Wood (1987) had similar interests in rejuvenator diffusion to Carpenter and Wolosick. The research described deviated from Carpenter and Wolosick's work in that a four layer staged extraction was performed. The researchers investigated three mixing scenarios. The RAP was tested using staged extraction with no introduction of rejuvenators. Rejuvenator with the RAP and heated it to 115.5°C (240°F) for 30 minutes to help induce diffusion into the RAP binder. The final mixture was a rejuvenated loose mix that was placed in an oven for 15 hours at 73.3°C (140°F). Trichloroethylene was used as the extracting solvent and each layer was dissolved in a 5-minute soaking increment. The solvent used to dip the mixture in was also divided into different volumes of 200, 200, 300, and 700 mL for washes 1 through 4 respectively. The authors outlined interesting findings with the RAP only sample. The outermost layer of the RAP was the hardest, with the second layer and third layer slightly softer but almost equal in penetration value. The innermost layer, however, was slightly harder. The authors attributed this to the fact that limestone in Indiana has a tendency to absorb the lighter

fractions of the binder. The authors concluded that the four rejuvenators that were tested only really worked on the outermost layers of the RAP. Those layers were tested to be closest to the AC-20 penetration grade binder in terms of the penetration test. The authors also note that the innermost layers were not significantly affected by the aging process.

1.4.3 Sequential Dissolution

Asphalt binder is commonly divided into different fractions. Petersen (2009) provided an insightful literature review on the oxidation characteristics of asphalt binders. In doing so he highlighted the division of asphalt into four fractions known as the Corbett fractions (Corbett 1969). These four fractions are saturates, naphthene aromatics, polar aromatics, and asphaltenes, each respectively increasing in molecular polarity. Each of these fractions reacts differently when introduced to an environment where oxidation can take place.

A more basic fractionation of the asphalt binder is its separation into two fractions, asphaltenes and maltenes. In this case, the maltene component is all non-asphaltene related fractions, which essentially consolidates three of the four Corbett fractions (Petersen 2009). Asphaltenes and maltenes are easily separated into fractions based on solubility in heptane. The *n*-heptane-soluble (C_7H_{16}) fraction is the maltene and *n*-heptane-insoluble fraction is the asphaltene. Liu et al. (1998) points out that an increase in asphaltene occurs due to the oxidation of some portion of the maltene phase. Many of

the studies with GPC have found similar results, with a decrease in the maltene fraction of the molecular weight distribution and an increase in the asphaltene fraction (Lu and Isacsson 2002, Siddiqui and Ali 1999, Kim and Burati 1993, Churchill et al. 1995, Lee et al. 2009a).

Work by Wang and Zhang (2010) voiced concern over the impact of solubility parameters, an indicator of how miscible materials are with each other, on the introduction of polymers into polymer modified bitumen. One effort made within their research is to evaluate the solubility of asphalt binder in 27 different solvents and evaluate the solubility parameter. Among these solvents were toluene and tetrahydrofuran. They tested the solvents on six different binders with penetration values ranging from 67 to 233 mm/10 at 25°C. Tests were performed by placing 0.5mg of binder in 5mL of solvent in a sealed test tube for 48 hours and then evaluating the solubility by way of microscopy. The researchers found that tetrahydrofuran was a good solvent for all binders and that toluene was a good solvent for all but one binder.

Concern has been raised over whether these solvents would preferentially dissolve certain binder constituents in a staged extraction scenario. This concern will henceforth be referred to as sequential dissolution. For example, when the initial wash is performed on the mixture, the lighter maltene fraction may wash out first, leaving behind asphaltenes which eventually break down from the outermost layer after successive washes. If this is the case, then the staged extraction method, while still useful, may not be truly removing

"layers" of binder, but rather fractions at different rates. This could influence data interpretation when comparing each layer. An example of the two cases is shown in Figure 1.4. Case 1 is that the binder is dissolved in layers, not sequentially. Case 2 is that the binder is dissolved sequentially by dissolving the maltene fraction prior to the asphaltene fraction.

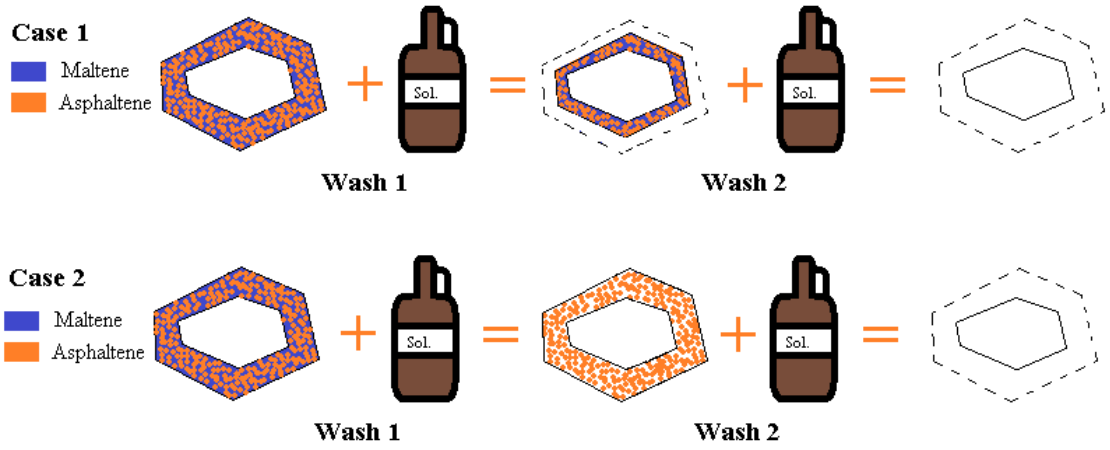

Figure 1.4 Removal of asphalt binder by layers versus sequential dissolution in solvent

One approach for evaluating the possibility of sequential dissolution is to consider the solubility parameters of the solvents and the bitumen along with its fractions. Hansen solubility parameters are used in chemistry as a 3 dimensional method of determining whether a material is soluble in a solvent. The three dimensions considered are the dispersion forces between molecules (δd), energy from dipolar intermolecular force between molecules (δp), and energy from hydrogen bonds between molecules (δh). This method is based largely on the common "like-dissolves-like" premise from basic chemistry. In 2004, Redelius set out to determine the solubility parameters of a

Venezuelan bitumen and its subsequent asphaltene and maltene fractions. Redelius calculated these parameters by using a large number of solvents with known solubility parameters. Redelius' work can be used to calculate an $(RA)^2$ value, which is defined as the distance between parameters in Hansen space. This equation (Equation 1.1), as defined by Hansen (2000) is:

$$(RA)^2 = 4(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2 \quad (1.1)$$

The parameter denoted by "1" is the parameter for the solute, while the parameter denoted by "2" is the parameter of the solvent. Contextually, the $(RA)^2$ value can be further used to calculate the relative distance between parameters, or RED. However, this requires a maximum solubility parameter difference which was not predefined. The concept of $(RA)^2$ is still relevant in the context that the lower the $(RA)^2$ value, the more soluble a material is in a given solvent. These values were calculated in the following Table 1.1 on the basis of Redelius' solubility parameters for bitumen, asphaltenes, and maltenes and Hansen's solubility parameters for the solvents of interest.

Table 1.1 $(RA)^2$ values calculated from Hansen solubility parameters provided in Redelius (2004) and Hansen (2000)

Solvent	**Bitumen**	**Asphaltenes**	**Maltenes**
Trichloroethylene (TCE)	4.2	11.1	15.5
Tetrahydrofuran (THF)	32.8	49.6	33.5
Toluene	9.5	20.0	20.0
Decahydronaphthalene (Decalin)	28.3	34.9	43.1
n-heptane	66.6	104.9	62.9

On the basis of Hansen solubility parameters, it appears that trichloroethylene is the best solvent for the bitumen with a $(RA)^2$ value of 4.2. Without considering *n*-heptane, the solvents rank as toluene, decahydronaphthalene, and tetrahydrofuran from best to worst respectively. A fractionation of the asphalt binder into asphaltenes and maltenes is typically conducted using *n*-heptane, which is why it is provided in this table. Examining the $(RA)^2$ values for *n*-heptane gives a relative difference between the asphaltene and maltene fraction, with a difference greater than 40 with the insoluble asphaltene fraction being the higher of the two values. With respect to the other common asphalt solvents, it appears that TCE may have a slightly higher dissolution rate for the asphaltenes than the maltene fraction and toluene has no difference between fractions. However, decahydronaphthalene appears to yield higher solubility for asphaltenes than maltenes, and THF has a large difference between the maltene and asphaltene fraction. Based solely on the solubility parameters for the given asphalt, it appears that THF would be a candidate for sequential dissolution of the asphalt binder, dissolving the maltene fraction prior to dissolving the asphaltene fraction.

1.4.4 Gel Permeation Chromatography (GPC)

Many works have been conducted that show the relationship between the chemical composition and the mechanical behavior of the asphalt binder. Gel Permeation Chromatography (GPC) is an analytical chemistry technique that yields the molecular

weight distribution of a given medium in solution. Figure 1.5 shows a simplified example of asphalt binder in solution passing through a single multi-pore GPC column.

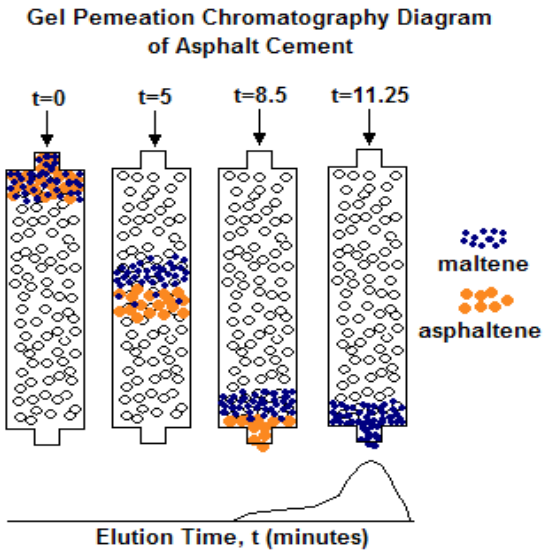

Figure 1.5 Example of Gel Permeation Chromatography

In Figure 1.5 the same column is represented four times at different elution intervals (t = 0, 5, 8.5, and 11.25 minutes) as shown on the x-axis. Time can be directly correlated to specific molecular weights on the basis of polymer standards such as polystyrene. The y axis is representative of the refractive index (RI) output in mV. An increase in refractive index indicates an increase molecules of a given size, with the maximum occurring where the most molecules of a given size are present. The example is based on the assumption that asphalt binder can be simply separated into two fractions; asphaltenes which are high in molecular weight and maltenes which are low in molecular weight. At t=0 the asphaltenes and maltenes are injected in one solution. However, as they pass through the column as represented by t=5 they begin to separate. This is due to the absorption of

smaller molecules by small pores in the columns packing. Larger molecules are able to pass these small pores, thus causing separation between the different molecular sizes. At t=8.5 the high molecular weight asphaltenes begin to exit the column and a slight increase in the RI occurs. At t=11.25 the asphaltenes have completely exited the column and the maltenes begin to exit. It is important to note that the peak of the chromatogram is at t=11.25, indicating that there are more molecules present of the correlating molecular size to t=11.25, which also corresponds to the region encapsulated by the maltenes fraction. Much work has been conducted studying the application of GPC to asphalt binder chemistry. The following Table 1.2 outlines many uses and findings:

Table 1.2 Overview of literature involving the application of GPC to asphalt binder

Citation	GPC Application
McCann et al. (2008)	Detected polymers in asphalt binders
Lu and Isacsson (2002) Siddiqui and Ali (1999) Kim and Burati (1993) Churchill et al. (1995) Lee et al. (2009a)	Studied effects of aging on asphalt binder using GPC
Snyder (1969)	Determined asphalt molecular weight distributions; based on polystyrene standard estimated between 700-2400 Daltons
Gilmore (1983)	Identified the presence of antistripping agents within asphalt cement
Kim et al. (2006)	Estimated RAP binder viscosity with GPC
Shen et al. (2007) Lee et al. (2006, 2009b) Daly and Negulescu (1997)	Studied effect of crumb rubber modification of binders
Kim et al. (2013)	Examined oxidative aging on polymer-modified asphalt mixtures made with Warm Mix Asphalt (WMA) technologies
Jennings et al. (1980, 1985a, 1985b) Yapp, Durrani, and Finn (1991)	Studied pavements ranging from good to poor condition and compared the chromatogram; established a tipping point within the chromatogram at which pavement failure occurs
Zhao et al. (2013a)	Correlated an increase in large molecular sizes to the complex modulus (G*) of binder

Many of the summarized works in Table 1.2 employed a measure of the Large Molecular Size (LMS) to compare the binders. The percentage of LMS grows as the binder is oxidized. Kim et al (2006) correlated the percentage of LMS directly to the binder viscosity, as stated above. This important finding relates LMS to the binder viscosity, a performance property of asphalt paving. The LMS is defined by the first 5 slices of the GPC chromatogram if the total chromatogram was divided into 13 equal slices on the basis of elution time as shown by Figure 1.6. The LMS% is defined with the following equation 1.2:

$$LMS\% = \frac{Area\ of\ first\ 5\ of\ 13\ slices}{Area\ of\ ALL\ 13\ slices} \quad (1.2)$$

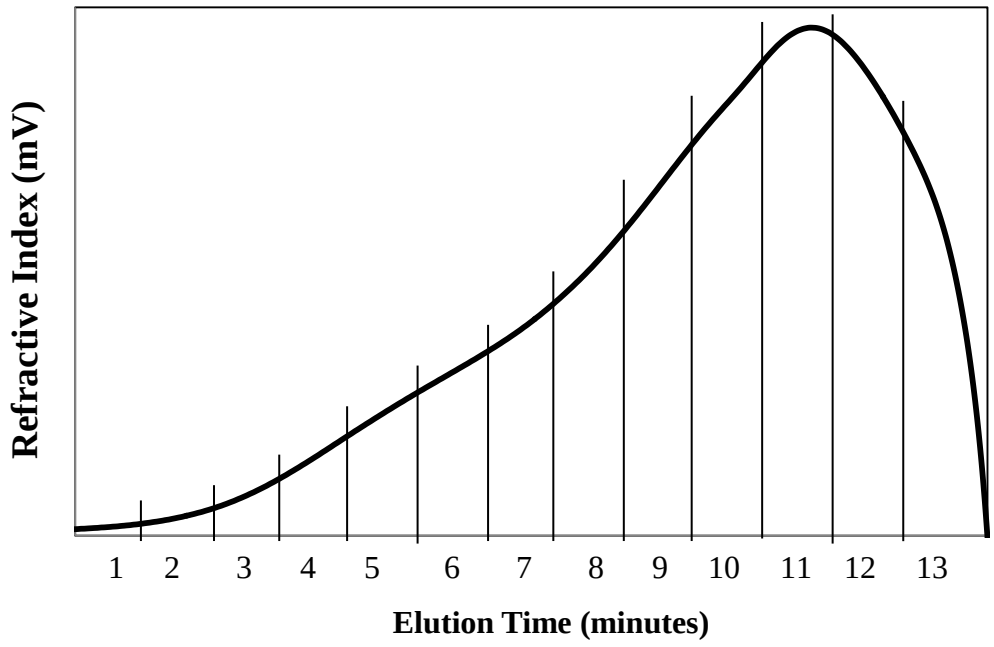

Figure 1.6 Chromatogram showing 13 slices

The following Table 1.3 shows varying opinions on the number of slices to evaluate in determining the true percentage of LMS. One will note that 5 is the most acceptable trend:

Table 1.3 Differing opinions on LMS percentage

Citation	Total # of Slices	Slices considered LMS
Asi, Al-Dubabi (1997)	12	n/a
Kim et al. (2006)	13	1-5
Churchill, Amirkhanian, Burati (1995)	10	n/a
Lee, Amirkhanian, Shatanawi (2006)	13	1-5
Doh, Amirkhanian, Kim (2008)	13	1-5

In 2013(a) Zhao et al. used LMS to estimate the complex modulus (G*) of asphalt binder that contained Recycled Asphalt Shingles (RAS) successfully. The researchers found that the complex modulus increased as the LMS% increased. Correlating these properties is important in further correlating the rheological properties of the asphalt binder to changes in the molecular weight distribution. This work is shown in Figures 1.7 and 1.8:

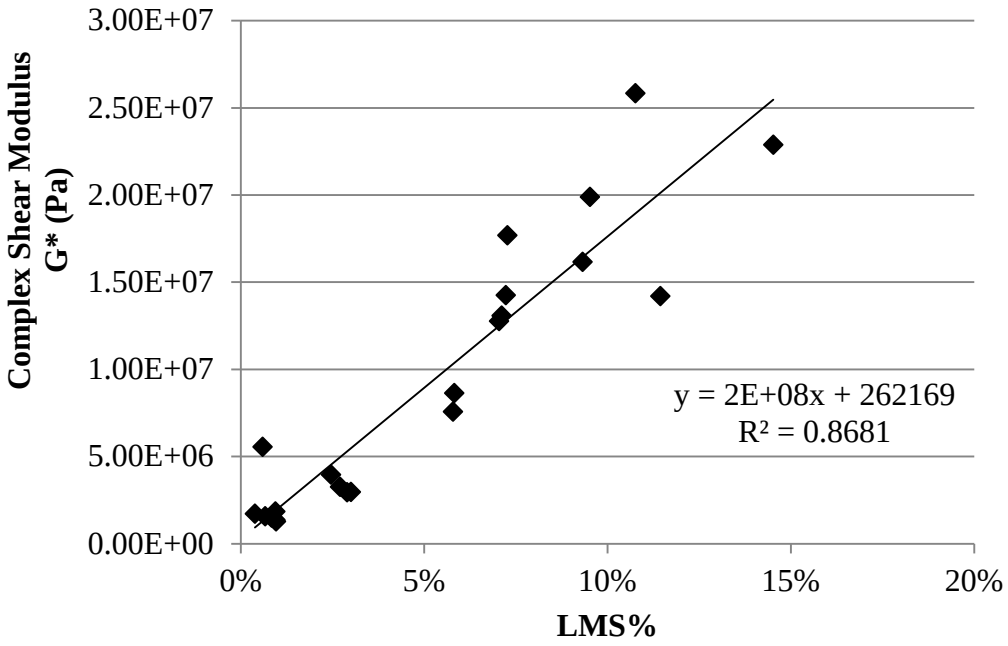

Figure 1.7 RAS at 25°C (Zhao et al. 2013a)

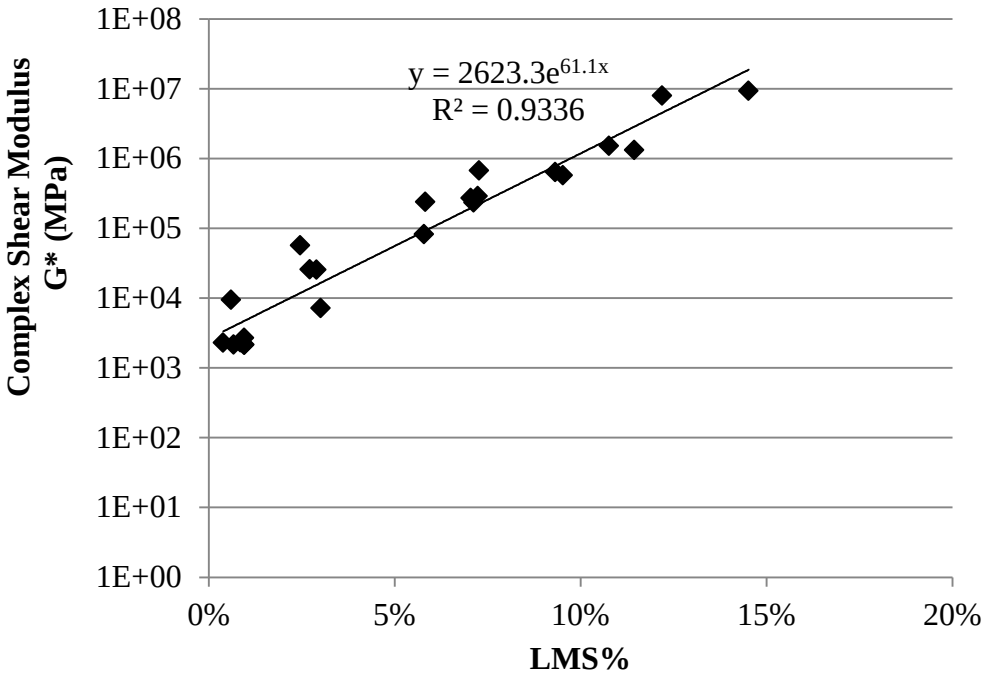

Figure 1.8 RAS at 64°C (Zhao et al. 2013a)

In 1980 Jennings et al. conducted research identifying a number of roadways in Montana and ranking them on the basis of the amount of cracking the pavement had in certain age ranges. If a pavement was less than 10 years of age and exhibited extensive cracking it was ranked as “bad”, newer than 10 years old and only had some cracks it was listed as “poor”, newer than 14 years with few cracks was considered “good”. Pavements that were considered “excellent” were those that were 14 years or older and had little cracking. Jennings noticed that as the ranking of the pavement declined (i.e. went from “excellent” to “bad”) the LMS% of the chromatogram continued to increase. However, Jennings also realized that the performance of the pavement was not based on asphaltene content, which generally takes up most of the LMS region.

Daly (2011) fractionated asphalt binder with heptane and then tested each fraction in the GPC compared to the total chromatogram. The asphaltene fraction is heptane insoluble, while the maltene fraction is soluble. Daly found that the asphaltene fraction was responsible for the LMS region, however it also tailed well into the maltene fraction. The maltene fraction was responsible for the remaining portion (e.g. the distribution after the LMS) of the chromatogram. In the case that the asphaltene fraction was solely responsible for the formation of cracks (i.e. stiffening of the binder) the asphaltene fraction would not drag on into the medium and small molecular size regions.

There are some perceived limitations of this methodology. Namely, when GPC is being used to identify molecular weight distributions the molecular weights are qualitative, not quantitative. Thus, as previously shown, to quantitatively analyze data the data needs to be normalized by dividing the area of the LMS region by the area of the total chromatogram. Furthermore, in effort to compare LMS percentages between samples the researcher must compare all samples with the same base limits. RAP for example typically will have more large molecules and those molecules will likely begin to elute from the column before the molecules of the virgin binder. Thus the minimum limits in which the area of the chromatogram is being analyzed need to be adjusted to meet those of the RAP (e.g. shifted from a minimum of 8.7 minutes for virgin binder to 8.5 minutes, which may be where the RAP begins to elute). See Appendix I for more information regarding the process of analyzing GPC data.

1.4.5 Fourier Transform Infrared Spectroscopy (FTIR)

A relatively new application for Fourier Transform Infrared Spectroscopy (FTIR) is its use in asphalt binder chemistry. FTIR is used to identify chemical functional groups within a medium. These functional groups are responsible for different characteristics of a complex compound. The principle of FTIR is sending an infrared beam containing many different wavelengths through a sample to measure what wavelengths the medium absorbs. These wavelengths indicate the presence of different functional groups. Figure 1.9 shows a diagram of a typical FTIR setup.

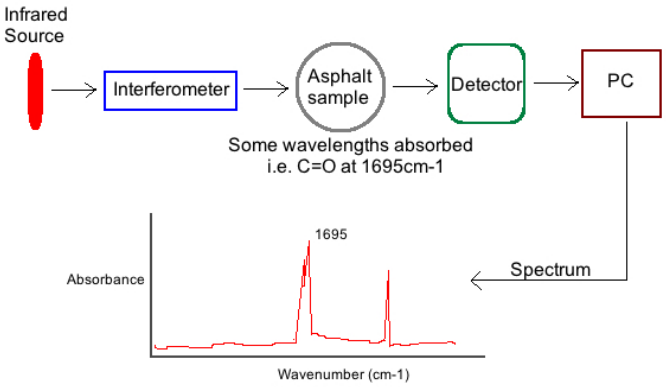

Figure 1.9 FTIR setup diagram

The concept of the FTIR instrument shown in Figure 1.9 can be described as follows: First, infrared beam passes into an interferometer. Though there are many types of interferometers, the most common is the Michelson Interferometer, thus it will be used to describe the FTIR processes. The interferometer contains a beam splitter at a 45 degree angle that divides the beam into half. One half of the beam is shined into a stationary mirror, while the other half is shined on a mirror that is constantly moving forward and

backward. After shining against the mirrors, the beam is reflected back at the beam splitter and recombined into one beam, which then shines through the sample. The moving mirror results in differing wavelengths than the stationary mirror. When the reflected beams are recombined, the path length differences between the beams cause constructive and destructive interferences, resulting in what is known as an interferogram. This interferogram exhibits a wide range of wavelengths. The combined beam is then passed through the sample which absorbs the wavelengths present in its infrared spectrum. The remaining interference passes into the detector, which can compile a number of interferograms, enhancing resolution. Upon detection, the interferogram is in time-domain space and is difficult to interpret by humans. By applying Fourier Transform to the interferogram one can convert the time-domain spectrum into a frequency-domain spectrum which is much easier to analyze and applicable to the study of the sample. The absorbed frequencies by the sample will be apparent through peaks that develop at the indicative wavelengths. Each of these is an identifier of the different chemical functionalities within the sample (Lampman et al. 2010).

In the case of asphalt binder chemistry, the major functional groups to monitor with respect to oxidation is the carbonyl (C=O) band found at 1695 cm^{-1} and the sulfoxide (S=O) group found at 1030 cm^{-1}. This growth in carbonyl is due to the introduction of oxygen causing the maltenes to become asphaltenes (Liu et al. 1998). The carbonyl band contains the ketone, carboxylic acid, and anhydride functionalities. Petersen (2009)

established that the growth of ketones is linearly related to an increase in the log viscosity of the binder, and his work in 1974 supports that most ketone formation is in the asphaltene fraction. Abbas et al. (2013) investigated the inclusion of RAS into binder and found that the carbonyl band may be a better indicator of aging because it seemed less variable than the sulfoxide band. Many other works have been published that emphasize the growth of the carbonyl band. These works are summarized in Table 1.4.

Table 1.4 Overview of literature involving the application of FTIR to study asphalt binder properties

Citation	FTIR Application
Lu and Isacsson (2002)	Evaluated differences between the thin film oven treatment (TFOT) and the rolling thin film oven treatment (RTFO) on the FTIR spectra. Examined carbonyl (C=O) and sulfoxides (S=O) peaks.
Ouyang et al. (2006)	Used FTIR-ATR (attenuated total reflectance) to study the effect of adding antioxidants to styrene butadiene styrene (SBS) tri-block copolymer modified asphalt during the oxidative aging process.
Huang and Grimes (2010)	Correlated FTIR spectra to viscous component of asphalt binder stiffening. Examined carbonyl and sulfoxide peaks.
Negulescu et al. (2006)	Examined SBS copolymer modified asphalt to gain understanding of oxidation and binder aging.
Abbas et al. (2013)	Studied changes of C=O and S=O peaks with the addition of RAS.
Yao et al. (2013)	Used FTIR to investigate microstructure changes in binder due to inclusion of nano-clay
Cong et al. (2012)	Investigated the effects of diatomite on binder properties with FTIR.
Fang et al. (2012)	Use FTIR to compare the aging mechanism of asphalt with and without packing waste polyethylene and waste rubber powder
Yut and Zofka (2011)	Study effects of aging on polymer modified binders with FTIR-ATR
Karlsson and Isacsson (2003)	Used FTIR-ATR to investigate the diffusion of rejuvenators into the asphalt binder

The work of Negulescu et al. (2006) was beneficial in identifying a normalizing peak between aged binder samples. The researchers found that the saturated C-C vibration band (also known at CH_2 and CH_3) found at approximately 1455cm^{-1} remained relatively constant before and after aging within binder of the same source and PG grade. This allowed for an aging index (AI) to be identified by using the following calculation (Equation 1.3):

$$Aging\ index\ (AI) = \frac{Area\ of\ Carbonyl\ (C{=}O)band\ at\ {\sim}1695cm^{-1}}{Area\ of\ Saturated\ C{-}C\ stretch\ band\ at\ {\sim}1455cm^{-1}} \quad (1.3)$$

As the area of the carbonyl region increase, so does the AI. This is reflective of an increase in oxidation of the binder which has been correlated to an increase viscosity (Huang and Grimes 2010).

1.4.6 Artificial RAP

Experimental design sometimes requires a laboratory aged, “artificial RAP”. This RAP is intended to be a controlled mixture with known source material. Examples of the need for artificial RAP were exemplified by Kowalski et al. (2009) in an evaluation of the impacts of varying percentages of RAP on frictional characteristics and a study conducted by Huang et al. (2005b) examining the impact of RAP on Portland Cement Concrete.

Studies that utilize artificial RAP often have different methods of laboratory aging. One common method is aging in a draft oven following a modified version of AASHTO R-30 "Standard Practice for Mixture Conditioning of Hot Mix Asphalt", though no true specification has been made. The following Table 1.5 outlines methods found in the literature for generating artificial, laboratory aged RAP:

Table 1.5 Summary of Artificial RAP methods

Reference	Methodology
Kvasnak et al. (2010) Kowalski et al (2009)	Followed AASHTO R30 but modified the long term aging portion of the specification by simply stirring a lose mixture twice a day during the duration of the specified aging period.
Huang et al. (2005b)	Aged a virgin mixture for 12 hours at 120°C in a draft oven
Bennert and Martin (2011)	Aged virgin mixtures for 2 hours in a draft oven at compaction temperature to simulate short term aging. Placed in an oven for 8 days at 100°C and stirred twice a day for long term aging.

The lingering question is if any of these methodologies truly simulate a true field aged RAP. Each approach has its own suggested method of aging, yet interestingly the standard method long term binder aging is presented in AASHTO R-28 which highlights the Pressure Aging Vessel (PAV) is never employed.

1.4.7 Unwanted Blending of Asphalt Contaminant in Fine Aggregates

Fine aggregate is a key component within asphalt pavement. It is responsible for helping achieve density and strength parameters as well as changing the rheological properties of

the mixture. As fine aggregate is introduced into a mixture the surface area increases. This increase in surface area will directly affect the asphalt content (Chapuis and Legare 1992). With optimum asphalt binder contents often ranging between 4-6% by volume, the unintentional addition of asphalt binder through the fines during the design phase could prove to be detrimental to the pavement structure. This may occur due to the contamination of the fine aggregate with asphalt binder that is not detectable to the naked eye.

Current specifications for measuring asphalt content are the AASHTO T-308 ignition oven method and AASHTO T-164 chemical extraction method. These two methods were found to not be useful when determining unknown asphalt presence in the realm of a fraction of a percent. The principle of the ignition oven method is to burn off binder at 578°C. However, one requirement of this specification is to perform correction factors on the aggregates which are going to be used in hot mix asphalt (HMA) due to burn off of "mineral matter". This is done by testing the mixture with a known asphalt content and calculating the mass loss beyond the asphalt burn off. However, if there is asphalt binder contaminant in the fine aggregate, it is impossible to tell the difference between the mass loss contributions of the asphalt binder and the mineral matter. Similar problems persist with the quantitative extraction method AASHTO T-164. Analogous to the ignition oven method, the mineral matter dissolvable in the solvent has to be accounted for through the ashing, centrifuge, or volumetric methods.

CHAPTER II

INVESTIGATION OF SEQUENTIAL DISSOLUTION OF ASPHALT BINDER IN COMMON SOLVENTS

A version of this chapter is in the process of being submitted for publication by Benjamin F. Bowers, Baoshan Huang, Qiang He, Xiang Shu, Xiaoyang Jia, and Brad Miller:

Bowers, B.F., Huang, B., He, Q., Shu, X., Jia, X., and Miller B.C. "Investigation of Sequential Dissolution of Asphalt Binder in Common Solvents."

Benjamin F. Bowers was the principle researcher and author of "Investigation of Sequential Dissolution of Asphalt Binder in Common Solvents". Benjamin's contribution was conducting all literature review, testing, data analysis, and writing the text contained in the manuscript. Dr. Baoshan Huang, Dr. Qiang He, and Dr. Xiang Shu provided guidance and ideas throughout the research process as well as editorial assistance. Bradley Miller and Dr. Xiaoyang Jia provided Benjamin with assistance in chemistry based laboratory experimentation.

2.1 Abstract

An investigation into the potential for sequential dissolution of asphalt fractions in a staged extraction scenario was conducted for common asphalt solvents. Asphalt cement is subjected to six sequential washes in trichloroethylene (TCE), tetrahydrofuran (THF), toluene, or decahydronaphthalene (decalin) were evaluated using Fourier Transform Infrared Spectroscopy (FTIR) and fractionated for asphaltene content. The results from the FTIR were evaluated statistically using a one-way analysis of variance (ANOVA) test and the solvents were found to induce no difference in mean carbonyl index. However, the fractionation of the asphalt cement after staged extraction showed that decalin and THF sequentially dissolved the asphalt cement while toluene remained suspect. Trichloroethylene does not appear to sequentially dissolve the bitumen fractions. The findings are in agreement with solubility calculations based on Hansen Solubility Parameters.

2.2 Introduction

Staged extraction in asphalt paving mixtures assumes thin layers of asphalt binder to be removed from around an aggregate during sequential exposures of an asphalt mixture to a solvent (Huang et al. 2005a). Staged extraction has been employed by some researchers to study the blending efficiency of Reclaimed Asphalt Pavement (RAP), the production of a predictable artificial laboratory aged RAP, as well as the diffusion of RAP rejuvenators (Huang et al. 2005a, Bowers et al. 2014a and 2014b, Zearley 1979, Carpenter and Wolosick 1980, Noureldin and Wood 1987). This technique employs the use of solvents to wash "layers" of binder off of a mixture to be analyzed. Each wash is between 30 seconds to 5 minutes long. After each wash, the binder solution is recovered and tested.

There are concerns about this technique particularly due to the use of solvents for binder layer removal. One theory is that the solvents may sequentially dissolve the binder in accordance to fraction. Corbett (1969) defines asphalt fractions to be the heavy asphaltenes, which are responsible for the stiffening properties of the asphalt binder, and the maltenes or petroltenes. The maltene/petroltene fraction of the binder contains saturates, polar aromatics, and naphthene aromatics. The concern with staged extraction is that the solvents may dissolve the light fractions of the binder first, followed by the heavier asphaltene fraction. In effect, this would result in the first "layer" of a staged extraction containing an unrepresentatively high level of light fractions as compared to the innermost "layers". From a performance perspective, this would mean that the

outermost “layer” (i.e. first wash) would likely be softer than the innermost “layer” (i.e. last wash), which could lead to a false characterization and understanding of the asphalt cement film around the aggregate. It is possible that the solvent dissolves the light fractions and leaves behind a skeleton-like structure of asphaltenes which eventually break down and dissolve into the solvent.

Redelius (2004) conducted a study that applied and defined the Hansen Solubility Parameters for a Venezuelan asphalt cement. The energy from dispersion forces between molecules (δ_d), energy from dipolar intermolecular force between molecules (δ_p), and energy from hydrogen bonds between molecules (δ_h) were considered from this research in order to calculate the potential quality of the solvents for the given asphalt. The distance between Hansen Parameters in Hansen space is referred to as “RA”. Hansen (2000) and Redelius take this approach a step further by calculating the RED, or relative distance by considering the R_M or maximum solubility parameter difference. However, in the context of this study the calculation of $(RA)^2$ yields enough insight into what the expected quality of these solvents will be. The $(RA)^2$ calculations are presented in Table 2.1 and the equation for calculating $(RA)^2$ is provided in Equation 2.1 as provided by Hansen (2000). Solvent based Hansen Parameters are considered from Hansen while the asphalt cement, asphaltenes, and maltenes Hansen Parameters are considered from Redelius’ work. The closer the RA value is to zero, the higher the quality of the solvent in terms of solubility with asphalt cement.

$$(RA)^2 = 4(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2 \quad (2.1)$$

Where $(RA)^2$ is the distance between Hansen Parameters, δ_d is the energy from dispersion forces between molecules, δ_p is the energy from the dipolar intermolecular force between molecules, and δ_h is the energy from the hydrogen bonders between molecules. The subscripts "1" and "2" next to each parameter in Equation 1 represent the parameter for the solute and solvent respectively.

Table 2.1 Calculation of the distance between Hansen Parameters $(RA)^2$ in Hansen space based on data from Redelius (2004) and Hansen (2000)

Solvent	Asphalt Cement	Asphaltenes	Maltenes
Trichloroethylene (TCE)	4.17	11.14	15.49
Tetrahydrofuran (THF)	32.84	49.61	33.5
Toluene	9.45	20.00	19.97
Decahydronaphthalene (Decalin)	28.33	34.92	43.13
n-heptane	66.61	104.88	62.93

The solvents explored in the research presented herein are presented in Table 2.1, with the addition of *n*-heptane for a reference to the reader. When fractionating asphalt cement, *n*-heptane can be used to dissolve the light maltene fraction of the binder because the asphaltene fraction is considered insoluble in *n*-heptane. The difference in solubility is displayed by the asphaltenes $(RA)^2$ value of 104.88 compared to the maltene $(RA)^2$ value of 62.93, substantially lower than that of the asphaltene. Redelius also notes the important fact that good solvents are defined by similar solubility parameters, while solvents with very different solubility parameters are considered poor solvents. The solubility parameters of the mixture match better with those of the solvent than the

parameters of each individual fraction's parameters, hence lower $(RA)^2$ values for the asphalt cement than each of the fractions. One of Redelius' findings is that asphaltenes may not be dispersed in maltenes as a colloid, but rather asphaltenes are soluble in the maltene fraction. If asphaltenes and maltenes are separated, they may tend to self-associate, creating stronger interactions than those formed between the two fractions when interacting with each other. Thus the solvent is more effective when breaking up the interactions between the asphaltenes and maltenes rather than the self-associated interactions. Further investigation into this theory would be beneficial; however it is not within the scope of this paper. Simply on the basis of asphalt cement solubility, TCE appears to be the strongest solvent, followed by toluene, decalin, and finally THF.

The objective of this study was to investigate the potential for the sequential dissolution of asphalt cement in common asphalt solvents using a staged extraction approach. To achieve this objective, highly oxidized, or aged asphalt binder was dissolved in trichloroethylene (TCE), tetrahydrofuran (THF), toluene, and decahydronaphthalene (Decalin) in six successive layers without the presence of aggregate. Each layer was then characterized using Fourier Transform Infrared Spectroscopy (FTIR). A fractionation was considered to separate the asphaltene and maltene/petroltene fractions for a comparison of the percent of asphaltenes present, providing insight to the question of sequential dissolution.

2.3 Materials and Methods

2.3.1 Asphalt Binder

A Performance Grade (PG)64-22 asphalt cement binder was used for investigation. The binder was subjected to short term aging using the Rolling Thin Film Oven (RTFO) following AASHTO T240-03. After short-term aging the binder was placed in a Pressure Aging Vessel (PAV) and long-term aged over two PAV cycles at 100C to ensure extreme oxidation. The binder was then blended and subjected to testing.

2.3.2 Solvents

Four solvents were investigated in the scope of this research. Each of these solvents has been historically used as an asphalt solvent. These include trichloroethylene (TCE), toluene, tetrahydrofuran (THF), and a solvent not-commonly used for asphalt studies, decahydronaphthalene (decalin). Decalin was used because it has similar solubility parameter to toluene (δ_T = 18.6 vs 18.2 respectively) and dissolution kinetics when it is used at a temperature of 15°C. This dissolution however is significantly slower than that of toluene due to the viscous nature of decalin.

2.3.3 Fourier Transform Infrared Spectroscopy Testing

A staged extraction method similar to that outlined by Huang et al. (2005a), Bowers et al. (2014a, 2014b), Jia et al. (2014), Zearley (1979), Carpenter and Wolosick (1980), and Noureldin et al. (1987) was used. The premise behind this method is that "layers" of binder are removed as the binder is washed in a solvent. For this experiment no aggregate was used so that the PAV aged binder was in a pure state, unaltered by the mineralogy of aggregate. A total of 20mg of binder was collected for each test. The binder was rolled into a sphere and placed into a copper basket. Six vials were filled with 10mL of fresh TCE, toluene, THF, or decalin, depending on which solvent was being investigated. The binder was then dipped into the each of the successive vials of solvent in 30-second increments, and allowed to sit in the last solvent until all binder was completely dissolved. The binders were then recovered in the vials using a rotary evaporator. The vials were then placed in a vacuum oven at 100°C over night to ensure that all of the solvent was evaporated from the binder.

FTIR samples were then drop-cast into films on potassium bromide (KBr) salt plates with toluene. The films were then placed in a vacuum oven for a minimum of 12 hours at 100°C to ensure the evaporation of the toluene. Films were then tested using a Nicolet 6700 FTIR. Data was processed using the OMNIC software that is standard with the equipment. Five sample replicates were used in testing.

2.3.4 Fractionation

An additional staged extraction procedure was performed on approximately 3 grams of binder. The PAV aged binder was dipped five successive times into approximately 100 mL of fresh trichloroethylene, toluene, or decalin. Each wash in trichloroethylene and toluene lasted 3 minutes and 20 seconds on the basis of total dissolution for 3 grams of binder in TCE. Instead of dipping a sixth time, as for FTIR testing, the remaining asphalt was placed onto a pan and oven dried under vacuum to remove any remaining solvent. The remaining binder was then fractionated for comparison to the control binder. The same time increments were used for toluene and THF. However, due to the significantly slower dissolution rate of asphalt in decalin, the time was adjusted to 26 minutes and 40 seconds per layer.

Fractionation was performed using soxhlet extraction, as shown in Figure 2.1. Iso-octane was used as the maltenes solvent and the binder was washed until the iso-octane around the extraction thimble was clear. The extraction thimble was then removed and dried in a vacuum oven over night. After drying the asphaltene fraction was massed and the ratio of asphaltenes to original total mass of binder before fractionation was calculated.

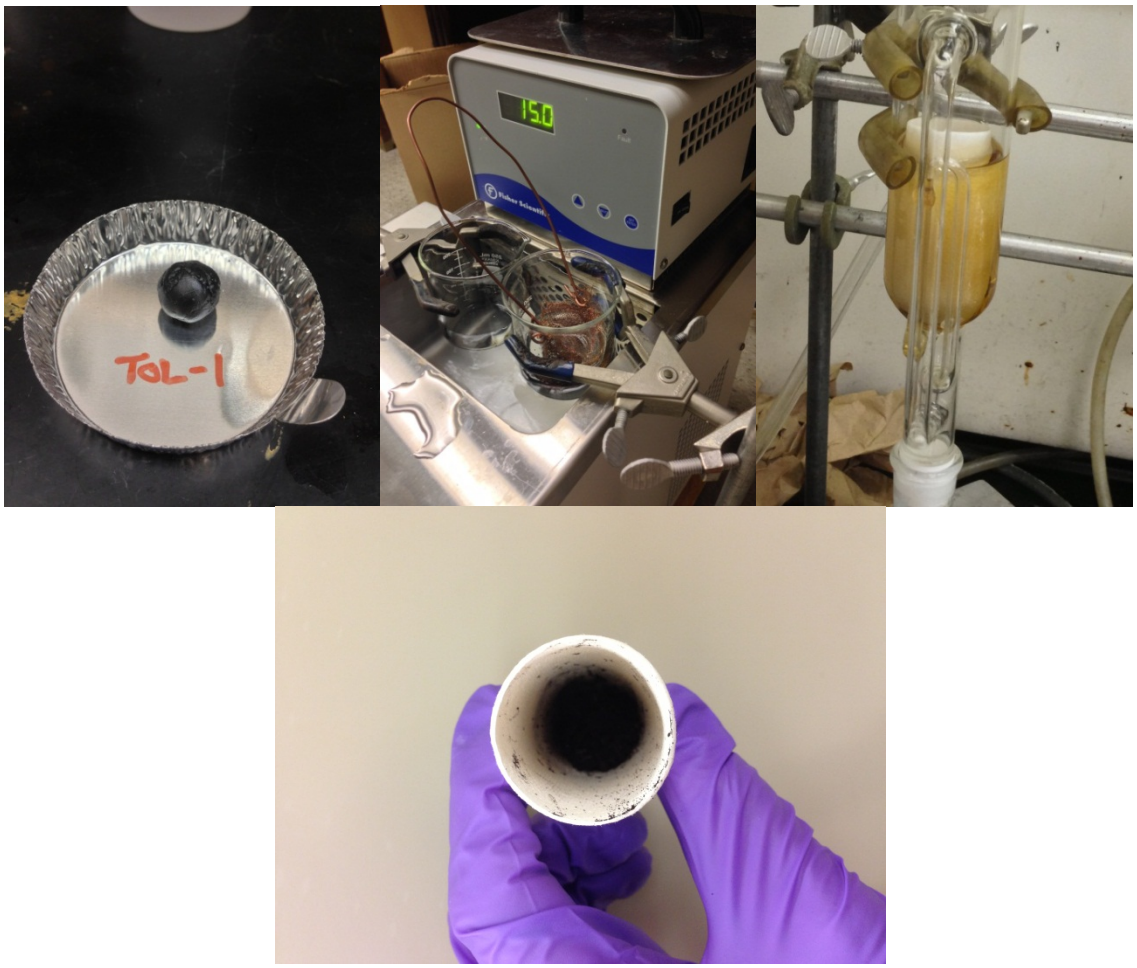

Figure 2.1 Top left: 3 gram ball of 2xPAV aged binder. Top Middle: Washing of binder (decalin) at 15°C. Top right: Soxhlet Extraction of remaining binder after 5 washes. Bottom: Asphaltene fraction after fractionation.

2.4 Results and Discussion

2.4.1 FTIR Analysis

Each layer of the material was evaluated by calculating a carbonyl index. This index, as described by Negulescu et al. (2006), Jia et al. (2014), and Bowers et al. (2014a, 2014b), measures the area beneath the carbonyl (C=O) band at 1695 cm^{-1} and the saturated C-C

band occurring at 1455 cm^{-1}. The ratio of this band (carbonyl divided by saturated C-C) is indicative of the aging that occurred within the binder, as presented in Equation 2.2. The saturated C-C band remains relatively constant and unaffected throughout the aging process, while the carbonyl band grows and more oxygen bonds are increased through the oxidation processes.

$$Carbonyl\ Index\ (CI) = \frac{Area\ of\ Carbonyl\ at\ 1695\ cm^{-1}}{Area\ of\ saturated\ C{-}C\ at\ 1455\ cm^{-1}}\ x\ 100 \qquad (2.2)$$

The approach for evaluating sequential dissolution was formulated on the basis of research conducted by Corbett (1969) and further outlined in the work of Petersen (2009). Petersen states that the various fractions, on the basis of Corbett fractionation, have different reactivity toward oxidation. Generally, during the oxidation process, there is a net reduction in the maltene fraction with an increase in the asphaltene fraction. This is important because the asphaltene fraction was ranked highest by Petersen (1974) in terms of ketone formation. On the basis of work by Petersen et al. (1993), Petersen (2009) notes the implications of the relationship between ketone formation and log viscosity in conjunction with the relationship between asphaltenes and log viscosity. The carbonyl band at 1695 cm^{-1} is indicative of ketone formation, among other functionalities. One can conclude that the ketone formation, and thus the formation of carbonyl functionalities within the binder, can be correlated to an increase in the asphaltene in the occurrence of sequential dissolution. Thus, if the binder is being sequentially dissolved and the maltene fraction is in effect releasing from the binder structure in solution prior to the asphaltene

fraction, an increase in carbonyl functionalities should be seen in the later stages of the staged extraction process. This conclusion is further supported by the work of Lin et al. (1995a, 1995b) which found that asphaltene content was directly responsible for the increase in the carbonyl functionality. Lin et al. went on to show that as maltenes are aged there is an increase in the asphaltene content due to the formation of asphaltenes. The researchers state that there is no difference between the asphaltenes that are present prior to aging or those which form during oxidation in terms of their impact on the "AFS", or asphaltene-carbonyl relationship, and that the un-aged maltene fraction had no distinctive carbonyl band.

Figures 2.2-2.4 show the carbonyl index for the asphalt binder in trichloroethylene, toluene, and tetrahydrofuran respectively. The means are provided with error bars representing one standard deviation above and below the mean.

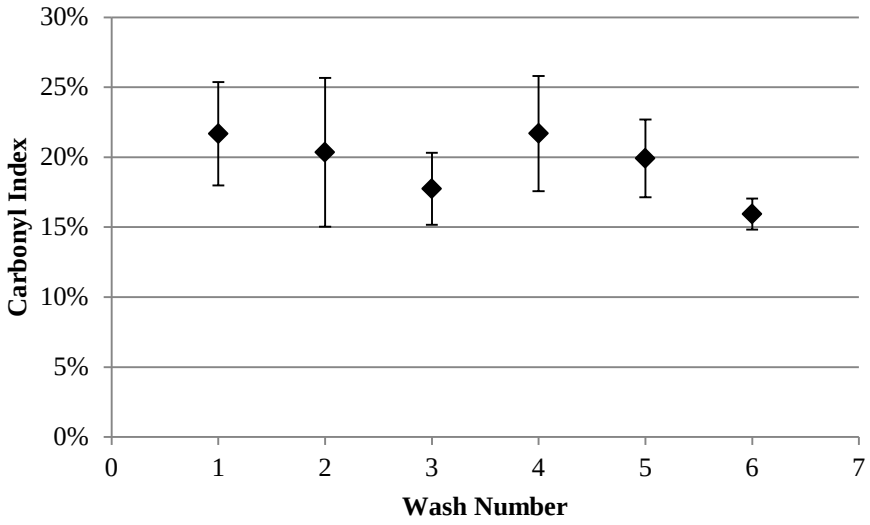

Figure 2.2 FTIR results for staged extraction of trichloroethylene (TCE)

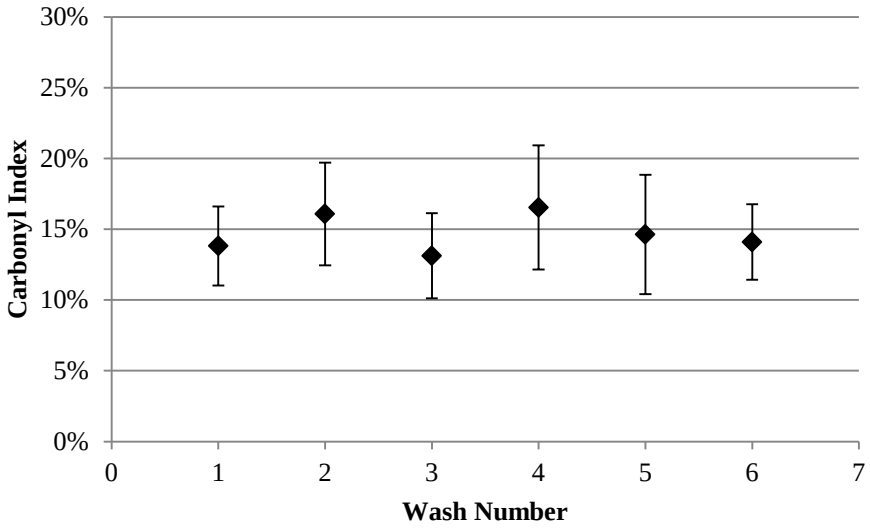

Figure 2.3 FTIR results for staged extraction of toluene

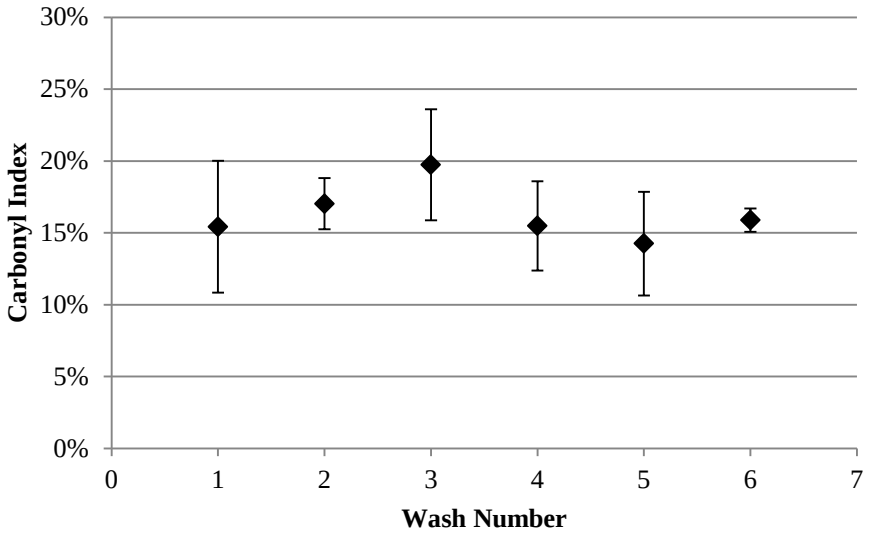

Figure 2.4 FTIR results for staged extraction of tetrahydrofuran (THF)

In order to further evaluate the data a one-way analysis of variance (ANOVA) test was conducted. The test considered a significance, α, of 0.05. Table 2.2 provides the p-values calculated based on the one-way ANOVA test.

Table 2.2 Solvent and p-values based on one-way ANOVA analysis with α=0.05

Solvent	**p-value**
Trichloroethylene (TCE)	0.086
Toluene	0.064
Tetrahydrofuran (THF)	0.186

The TCE sample had a resulting p-value of 0.086, slightly above the α = 0.05. The final data point is likely the cause of this close p-value. The toluene samples produced a p-value of 0.634, which shows that there is no significant difference between means. The THF solvent has a p-value of 0.186, also significantly higher than the α = 0.05.

The null-hypothesis that there was no difference in mean values was found to be true by way of the one-way ANOVA analysis. On the basis of carbonyl index, the fact that there is no difference in means indicates that there is no occurrence of sequential dissolution. If sequential dissolution had occurred, it is expected that there would be a significant variability in the mean values because the maltene and asphaltene fractions would not remain the same.

2.4.2 Fractionation Results

In order to further evaluate the potential of sequential dissolution in the given solvents, a fractionation was performed after the staged extraction method was utilized. Before any solvent testing occurred a control test was performed in triplicate on the binder to establish repeatability and to get a baseline asphaltene content (%) for comparison to the other solvents. The control fractionation was conducted on a binder that had not yet come into contact with any solvent. Upon completion of the control and establishment of repeatability, each binder sample was washed five times in the solvent of interest. The remaining binder after five washes was then fractionated rather than washing it a sixth time and completely dissolving it. The basis of this procedure is that if the binder was in fact sequentially dissolving there should theoretically be larger asphaltene fraction left after all prior washes had taken place. The following Figure 2.5 shows the resulting asphaltene contents after fractionation:

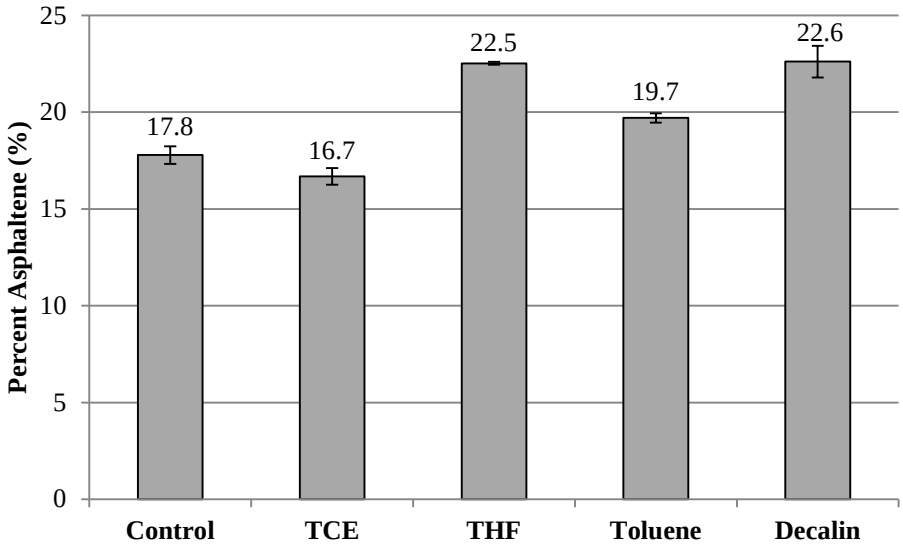

Figure 2.5 Asphaltene percentages for the binder exposed to each solvent.

The control fractionation yielded an average asphaltene content of 17.8%. This value is reasonable on the basis of Yang, Cong, and Liao (2003) who performed a study applying solubility theory to the evaluation of aging asphalts. The researchers found that their asphalts exhibited asphaltene contents in the upper teens to lower twenties when using *n*-pentane and *n*-heptane to determine asphaltene content. Trichloroethylene, which according to the solubility parameters provided by Redelius (2004) and Hansen (2000) should be the most compatible of all tested solvents with an $(RA)^2$ value of 4.17 yielded an asphaltene content of 16.7%, just below that of the control mixture. The $(RA)^2$ values calculated on the basis of Redelius' (2005) work indicates that the asphaltene fraction is slightly more soluble in TCE than the maltenes fraction with $(RA)^2$ values of 11.14 and 15.49 respectively. This may suggest why the asphaltene fraction is slightly lower in the TCE washed sample than in that of the control.

According to the solubility parameters Toluene should be the second best solvent with a $(RA)^2$ value of 9.45. Toluene yielded an asphaltene content of 19.7, nearly 2% higher than the control. This may be within the range of statistical variability, but could also be hinting at the possible sequential dissolution of the binder. However, toluene does have solubility parameters for both the maltene and asphaltene fraction that are very similar, which suggests that sequential solubility should not occur.

The fractionation of the decalin yielded an asphaltene content of 22.6%, which is significantly higher than that of the control. This indicates that sequential dissolution is occurring. Decalin has a similar total Hansen solubility parameter as toluene. However, because the kinetics are significantly slower, it should have similar dissolution properties as toluene. The fact that decalin exhibits sequential dissolution over an increased time suggests that the toluene may be sequentially dissolving the binder as well. The decalin $(RA)^2$ values are not that dissimilar between maltenes and asphaltenes (43.13 and 34.92 respectively), yet there is clearly more of the asphaltene fraction present after 5 washes with solvent. This is a cause of concern for the use of toluene and decalin as a solvent for staged extraction. However, this relationship highlights the potential impact of shortened wash times for stronger solvents. Toluene, which has a significantly faster dissolution time than decalin, shows very little difference in asphaltene content. This could be because the time it takes for a layer to be removed does not allow sufficient time for a separation between the percentages of dissolved maltenes versus dissolved asphaltenes to occur.

Tetrahydrofuran exhibited the second highest asphaltene fraction of the four solvents represented with a value of 22.5%. This is not surprising considering the $(RA)^2$ value for the maltenes fraction is 33.50, much lower than the asphaltene fraction at 49.61. The results are in agreement with the calculated $(RA)^2$ values and THF is found to not be a strong solvent candidate for staged extraction.

2.5 Conclusions

The solvents trichloroethylene, toluene, tetrahydrofuran, and decahydronaphthalene were evaluated for their potential to sequentially dissolve asphalt binder in a staged extraction process using FTIR and fractionation. The following conclusions can be reached:

- Sequential dissolution does exist for most of the tested solvents
- Trichloroethylene works best for staged extraction experiments
- In accordance to the FTIR results and ANOVA analysis there is no difference in the mean carbonyl index for TCE, toluene, or THF.
- Decalin exhibits characteristics expected for sequential dissolution with a significantly higher asphaltene content than that of the control
- Similarities in binder kinetics between decalin and toluene make the increased asphaltene content in toluene suspect for sequential dissolution, however this may show the impact of short wash times

- THF exhibits characteristics expected for sequential dissolution which further supports the application of Hansen Solubility Parameters as an evaluation mechanism for asphalt cement fraction solubility

2.6 Acknowledgment

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CHAPTER III

INVESTIGATION OF RECLAIMED ASPHALT PAVEMENT BLENDING EFFICIENCY THROUGH GPC AND FTIR

A version of this chapter has been published by Benjamin F. Bowers, Baoshan Huang, Xiang Shu, and Brad C. Miller:

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Benjamin F. Bowers was the principle researcher and author of "Investigation of Reclaimed Asphalt Pavement Blending Efficiency through GPC and FTIR". Benjamin's contribution was conducting all literature review, testing, data analysis, and writing the text contained in the manuscript. Dr. Baoshan Huang and Dr. Xiang Shu provided guidance and ideas throughout the research process as well as editorial assistance. Bradley Miller provided Benjamin with assistance in chemistry based laboratory experimentation.

3.1 Abstract

Due to economic and environmental considerations, reclaimed asphalt pavement (RAP) has been frequently included into asphalt paving mixtures during pavement construction and maintenance activities. Many studies have been conducted with regard to the effect of RAP inclusion in the pavement structure and its mechanical performance, yet the blending efficiency of the RAP and virgin binder is still unknown. It is often assumed that a complete blend between the RAP binder and virgin binder does occur. However, if there is not a complete blend concerns arise that the long-term pavement life could be compromised. In this study, staged extraction is performed on an asphalt mixture blend on the premise that individual layers of asphalt binder can be removed from the mixture until all that remains is the aggregate. Each binder layer is then tested and compared quantitatively using Gel Permeation Chromatography (GPC) and Fourier Transform Infrared Spectroscopy (FTIR) to identify the extent to which RAP and virgin binder

blend. Results of this study have shown that a certain degree of blending does occur throughout all layers of the mixture.

3.2 Introduction

A popular topic among the asphalt industry is the efficiency of Reclaimed Asphalt Pavement (RAP) binder as it is blended with new virgin binder in a paving mixture. The asphalt binder in the RAP stiffens during its service life due to oxidation processes, which can lead to fatigue cracking and other performance issues. Oxidation occurs during the pavement mixing process as well as due to environmental exposure. Past research has shown that RAP can have both beneficial and negative effects on a pavement mixture. Many works have found that RAP increases rut resistance, decreases moisture susceptibility, and increases tensile strength. However, research has also shown that RAP inclusion can have a negative effect on the fatigue resistance of the mixture (Huang et al. 2005a, Shu et al. 2012, Shu et al. 2008, Zhao et al. 2012, Zhao et al. 2013b).It is commonly accepted that when RAP is heated, the viscosity of the binder on the RAP aggregate is reduced, thus allowing blending to occur with new virgin binder. Past research on this topic has found that there is a variation of blending that may occur dependent upon the amount of RAP in the mix. For example, it is suggested by Kandhal and Foo (1997) that when 15% RAP is added to a mix, no change in binder grade is necessary. However, between 15 and 25% RAP addition, the high and low temperatures of the virgin binder grade must be reduced by one SuperPave performance grade (PG)

increment. When above 25% RAP is introduced to the mix, a blending chart is required for determining what binder grade of virgin asphalt cement (AC) should be used.

One recurring theme in RAP research is the belief that the particle actually behaves as "black rock" where the reclaimed binder is bonded to the reclaimed aggregate and is too stiff to be blended at mixing temperature (Soleymani et al. 2000, Huang et al. 2005a, McDaniel et al. 2000). The implications of this theory are that there is no virgin and reclaimed binder blending within the mixture. If no blending occurs the use of blending charts in asphalt pavements including RAP are no longer applicable (Huang et al. 2005a, McDaniel et al. 2000). The findings of *NCHRP 9-12 Recommended Use of Reclaimed Asphalt Pavement in SuperPave Mix Design Method* indicate that a partial blending does occur to a significant extent. McDaniel et al. and Mogawer et al. both evaluated blending efficiency using the "Bonaquist approach" which uses recovered binder and mixture volumetrics in the Hirsch Model to estimate the dynamic modulus. This estimated dynamic modulus is assumed to be on that of a perfect blend due to the mixing of the binders in solution. If 100% blending occurs the dynamic modulus of the mixture should match that of the estimated dynamic modulus with statistical significance (McDaniel et al. 2012, Mogawer et al. 2012). Navaro et al (2012) showed that different mixing temperatures can vary the amount of binder blending that occurs by evaluating mixtures with UV and white light microscopy. The researchers concluded that a reduction in testing temperature by 30°C could increase the required mixing time for the same quality of blend by two or three fold. Shirodkar et al. (2011) attempted to identify the degree of

partial blending that occurs by evaluating ratios of G*/Sinδ for different percentages of RAP blended with different binder performance grades. The researchers concluded that at 25% RAP content PG70-28 blends up to 70% and at 35% RAP content PG 58-28 blends up to 96% for their given gradation and mixing methods. The researchers applied this knowledge to further develop a procedure for determining proper blending charts for partial blending (2013). A method must be developed to further examine all current theories of RAP blending efficiency.

3.2.1 Staged Extraction

Huang et al. (2005a) describes a composite system which may exist in RAP coated with virgin asphalt cement. This system would exist because the stiff (aged) binder on the RAP aggregate could not effectively blend with the virgin aggregate. Thus, Huang et al. initiated a study which evaluated this hypothesis by staged extraction of the asphalt binder from the RAP aggregate. RAP, which had been blended with virgin AC, was immersed in trichloroethylene (TCE) solvent for 3 minutes, then immersed in a second beaker of TCE, and so forth until 4 batches were complete. Each wash with TCE removed individual “layers” from the RAP, with the layers ranging between 1 and 2 microns in equivalent film thickness. The binder was then recovered and studied with a dynamic shear rheometer (DSR) and Finite Element Analysis. The study found that staged extraction may be used to evaluate asphalt cement coated aggregates, a composite does form, and that the original binder around the RAP particle actually stiffens.

A similar study was conducted in 1979 by the Iowa Department of Transportation in which 6 samples were taken from asphalt pavements, some of which contained RAP. Then penetration tests were performed on recovered asphalt. The asphalt samples were recovered by using reagent grade TCE and washing the asphalt mixture twice. The penetration results for both layers were approximately the same, and in some cases the second layer (closer to the aggregate) yielded higher values. This was attributed to the presence of large amounts of shale in the aggregates, which has selective absorption of the lighter asphalt fractions, thus yielding higher penetration asphalt in the second layer. A laboratory mix was also created using an aggregate coated with 60 penetration asphalt that was age hardened in an oven. A 200 penetration asphalt was then coated onto the mixture at the lowest possible temperature to observe whether blending occurred. Three extractions were performed on the same mixture sample, yielding three layers. The penetration values were well below 200 found that the outer layer began to get stiffer while the inner layer softened until the penetration values were nearly identical between layers. The authors concluded that the rejuvenator diffused through the RAP binder over time. Noureldin and Wood [17] also investigated rejuvenator diffusion with a staged extraction method, but instead of using a 2 layer system the researchers investigated a 4 layer system. The researchers looked at adding three different rejuvenators with and without virgin aggregate, as well as analyzed RAP without any rejuvenator using penetration and viscosity tests. When analyzing RAP, the researchers found that the outermost layer was very stiff, with the second and third layers unchanged. The

innermost layer was stiffer than the second and third layers, which the authors attributed to the tendency of limestone to absorb the light fractions of the binder.

Some concern has been generated with regard to the possible quasi-selective dissolution of the asphalt binder in a staged extraction method. The premise of this discussion is that perhaps the solvent used in staged extraction does not extract true “layers” of binder from the mixture, but rather extracts various fractions of the binder molecules at different rates in accordance to their solubility in the extraction solvent. The exact kinetics of dissolution for all the various chemical constituents are not known and cannot be assessed within the scope of this study. However, a successful attempt to validate the methodology was made and is outlined herein. Given that previous work using the staged exaction method in a strong solvent is in agreement with accepted theory, the use of a "layer stripping" model is appropriate for the purposes of this study. The penetration values were well below 200, which meant that the 200 penetration asphalt was indeed blending with the age hardened 60 penetration asphalt (Zearley 1979). Carpenter and Wolosick (1987) applied the same technique as Zearley to study the effect of rejuvenators on RAP. RAP was heated to 116°C and mixed with 20% rejuvenator/modifier. Samples were then dipped for 3 minutes in TCE in two layers. The binder was then recovered and tested with the Penetration Test. The researchers found that the penetration levels were different for the two layers with the outermost layer having a higher penetration value than the innermost layer. However, the same mixture was extracted and tested again after it was allowed to sit for a period of time and it was

3.2.2 Asphalt Chemistry

Due to the many sources of crude oil as well as differences in the refining processes, asphalt is difficult to characterize chemically. Asphalt is made up largely of hydrocarbons, along with other molecules and molecular structures. These molecules generally consist of carbon, hydrogen, sulfur, oxygen and nitrogen, as well as a traceable amount of metals. Chemically speaking, asphalt can be divided into four major fractions: saturates, naphthene aromatics, polar aromatics, and asphaltenes (Petersen 2009). With that in mind, there has still been significant research dedicated to the study of asphalt chemistry. Because asphalt is similar in nature to polymers, there have been many approaches taken that are similar to that of polymer testing and analytical polymer chemistry. The two polymer chemistry techniques outlined in this manuscript for the study of polymer testing are Gel Permeation Chromatography (GPC) and Fourier Transform Infrared Spectroscopy (FTIR).

3.2.3 Gel Permeation Chromatography

Gel Permeation Chromatography, also known as Size Exclusion Chromatography (SEC), is used to separate the molecules of a solution into its various sizes, yielding a clear depiction of the molecular weight distribution within the medium. Many researchers have applied it to the study of asphalt chemistry, and studies focus primarily on polymer modified asphalt binders and the aging mechanism of asphalt cement.

The use of Gel Permeation Chromatography for asphalt chemistry dates as far back as the 1960's. In 1969, R.L. Snyder described GPC as a "quick way" to find molecular separations in asphalt. Based on a polystyrene standard, he found values of average molecular weight in the 700-2400 Dalton range (Snyder 1969). More recently, Bowers et al. (2013) used GPC as a method of detecting asphalt in fine aggregate particles by examining the molecular weight change. Other work was conducted by Jennings et al. (1980) in which a number of roadways in Montana were studied. Jennings found that, based on a primitive asphalt rating system, the "worse" the asphalt pavement was with respect to damage, the higher the number of large molecules (LMS) present in the asphalt. He also concluded that asphaltene presence alone was not enough to predict performance accurately. In 1985 Jennings et al. published another work in which the researchers found that there seemed to be a tipping point with respect to percent LMS in which the LMS becomes detrimental (Jennings et al. 1985a, 1985b). The researchers stated that the tipping point seems to be around 20% LMS (Yapp et al. 1991).

The concept of large molecular size (LMS) increase with respect to the stiffening of asphalt binder due to oxidation and aging is a popular one. The following table (Table 3.1) shows a number of the different approaches to LMS. Each argues that the chromatogram needs to be divided into slices and then integrated, but there is variation on the number of slices that need to be used. One could theoretically use a range of molecular weights to divide the chromatogram. Evaluating the chromatogram on the basis of integration is straight forward, and a vast majority of the literature that studies

similar GPC applications to the study of asphalt binder oxidation have been proven statistically significant with the use of an integrated LMS method.

Table 3.1 Differing opinions on LMS percentage

Researchers	Total # of Slices	Slices considered LMS
Asi, Al-Dubabi (1997)	12	n/a
Kim et al. (2006)	13	1-5
Churchill, Amirkhanian, Burati (1995)	10	n/a
Lee, Amirkhanian, Shatanawi (2006)	13	1-5
Doh, Amirkhanian, Kim (2008)	13	1-5
Zhao et al. (2013a)	13	1-5

Some of the most convincing results reflecting the effects of LMS percentage on aging and oxidation are presented in the work of Kim et al. (2006). The researchers aged asphalt samples and tested the absolute viscosity and LMS% for comparison. A correlation between the LMS percentage and the absolute viscosity was determined using statistical regression models. The researchers conclude that as the percentage of LMS goes up, there is an increase in the absolute viscosity and thus a stiffening of the asphalt binder in the mixture. Zhao et al (2013a) correlated the complex modulus, G*, of virgin asphalt binder blended with reclaimed asphalt shingles (RAS) binder to the percent LMS. The researchers analyzed the first 5 of 13 slices of the GPC chromatogram as LMS and correlated using regression analysis.

3.2.4 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is a method of determining chemical functional groups within a medium. Chemical functional groups are groups of atoms which are responsible for different reactions within a compound. Lu and Isacsson (2002) studied the effects of aging on bitumen chemistry and rheology. Included in this study is GPC. Asphalt samples were aged with thin film oven treatment (TFOT) and rolling thin film oven treatment (RTFOT). It was found that the C=O double bond, also known as the carbonyl region, changed very little when comparing TFOT and RTFOT. It is however stated that the carbonyl peak along with the S=O sulfoxides peak tend to grow as the material is aged.

Many works have focused on the use of FTIR-ATR (Attenuated Total Reflectance). FTIR-ATR is very similar to FTIR, but primarily examines the surface of the medium. This is a beneficial technique because it requires little to no sample preparation. Ouyang et al. (2006) studied the effects of adding antioxidants to styrene butadiene styrene (SBS) tri-block copolymer modified asphalt during the oxidative aging process. By use of FTIR-ATR they found an increase in the carbonyl group as the asphalt binder aged. The researchers also found a resistance to growth in the carbonyl group with the addition of the antioxidants to the mixture.

Huang and Grimes (2010) conducted research at the Western Research Institute with the objective of correlating FTIR results to the viscous component of asphalt stiffening. By

testing asphalt binders from different sources at different temperatures and aging periods they found that initially the asphalt binder viscosity stiffened rapidly, but then progressed at a slower rate. Additionally, it was found that asphalts from different sources, though the same performance grade, age differently. As stated in past research, it was found that the carbonyl and sulfoxide functional group's increased with aging time, however the sulfoxide group decreased after 507 hours of aging. This is understood by the authors to have been caused by a transformation into sulfones during the PAV aging process. Interestingly, the authors were able to correlate the rheological shift factor to an increase in the carbonyl peak to a $R^2 = 0.95$. Petersen (2009) also states that the increase in ketones, present in the carbonyl functionality, is log linearly related to an increase in viscosity.

Further research was conducted by Negulescu et al. utilizing FTIR to analyze SBS copolymer modified asphalt cement (2006). In the study, the researchers used FTIR to gain a relative understanding of oxidation, which is directly related to asphalt binder aging. It was observed that the carbonyl band increased as compared to the saturated C-C vibrations. The area of the carbonyl absorbance occurring at $1695cm^{-1}$ could be compared to that of the C-C absorbance occurring at $1455cm^{-1}$. The ratio of the C=O and C-C vibrations could give a relative comparison of how much oxidation is occurring. As the ratio increases there is a higher level of oxidation in the asphalt binder, and thus a stiffening of the binder.

The objective of the present study is to explore the blending efficiency of RAP within asphalt paving mixtures. The staged extraction method was implemented to study the binder layering system before and after mixing. GPC and FTIR were considered to investigate each layer and determine the binder blending that occurs on the basis of the molecular and chemical characteristics defined by the aging processes.

3.3 Experimental Methodology

The laboratory experiment utilized GPC and FTIR to investigate the differences in the virgin mixture, field collected RAP, and RAP blend. For comparing the FTIR and GPC tests a controlled artificial RAP blend was used. The testing is outlined in Table 3.2 and the following specific problems are addressed:

- Whether staged extraction dissolves asphalt binder through a “layered” sequence, i.e. from the outside to inside layers in an asphalt-aggregate composite.
- Can FTIR and GPC be used to differentiate the molecular weight and oxidative characteristics of each “layer” in the composite system, allowing the ability to evaluate the blending efficiency of the RAP and virgin binders.

Table 3.2 Outline of Test and Mixture comparisons

	Test	**Mixture**	
Test Comparison	GPC	Artificial RAP Blend	
	FTIR	Artificial RAP Blend	
	GPC	Virgin Mixture	**Mixture Comparison**
	GPC	RAP	
	GPC	RAP Blend	

3.3.1 Materials

This study was conducted using PG64-22 virgin binder as well as RAP from an unknown source. Two mixes were created for GPC testing. A virgin mix was created using virgin aggregate, heated to 160°C, and 6% virgin PG64-22 asphalt binder heated to 130°C by mechanically mixing. The RAP blend was created using 6% asphalt binder, PG64-22 virgin asphalt binder, and was created with a 50-50% of virgin aggregate retained on the 4.75 mm (#4) sieve and RAP passing a 4.75 mm. (#4) sieve. The RAP contained 6% asphalt binder and was accounted for in the final mix. Using smaller RAP screens allowed for the RAP particles to be separated from the mixture and tested. This lowers the risk of testing virgin particles and thus retaining potentially inaccurate results.

Due to the dependency of the same binder source and grade for the FTIR comparison an artificial RAP was created. PG64-22 binder was short term aged in the rolling thin film oven (RTFO) followed by two 20 hour cycles in the Pressure Aging Vessel (PAV) at 100°C. The PAV aged asphalt was then mixed at 180°C with 9.5 mm. (3/8 in.) gravel at an asphalt content of approximately 6% by mass. The mixing lasted 2 minutes and a HOBART A200 tabletop mixer was used.

3.3.2 Staged Extraction

Trichloroethylene (TCE), a common asphalt solvent, was used for staged extraction. A small copper mesh basket was created for dipping the asphalt sample into the TCE. Four

beakers were filled with approximately 50mL of TCE. Each beaker was placed on a stir-plate with a micro-stir bar to agitate the solvent. Approximately 25 grams of material was then placed into the copper basket. Twenty-five grams was selected to provide enough individual particles for each sample batch to decrease any possible influence of asphalt binder film thickness variability on the aggregate. The test began by immersing the mixture into TCE for 30 seconds, 1 minute, or 3 minutes. After the allotted time, the basket and mixture were removed and immediately placed into the next beaker of fresh TCE and allowed to sit for the same amount of time. This step was repeated until the fourth beaker of fresh TCE. The basket and mixture remained in the fourth beaker for a minimum of the allotted time period. However, when the mixture was removed it was visually inspected for any remaining asphalt binder on the aggregate. If asphalt binder could be seen, the basket and mixture were placed back into the fourth beaker until no asphalt binder could be visually detected on the aggregate. Each of the four beakers contained an asphalt binder/TCE solution which is constituted as one “layer”. The solutions were then removed from the beaker and placed into a labeled scintillation vial with a Teflon lined cap.

3.3.3 Rotoevaporation

Rotoevaporation was used to recover the asphalt from solution which was in a 20 mL scintillation vial. The water bath used to heat the solution was 70°C. After all noticeable

solvent was evaporated from the vial, the vial was placed in vacuum-oven overnight at 80°C to remove any remaining solvent within the mixture.

3.3.4 Gel Permeation Chromatography

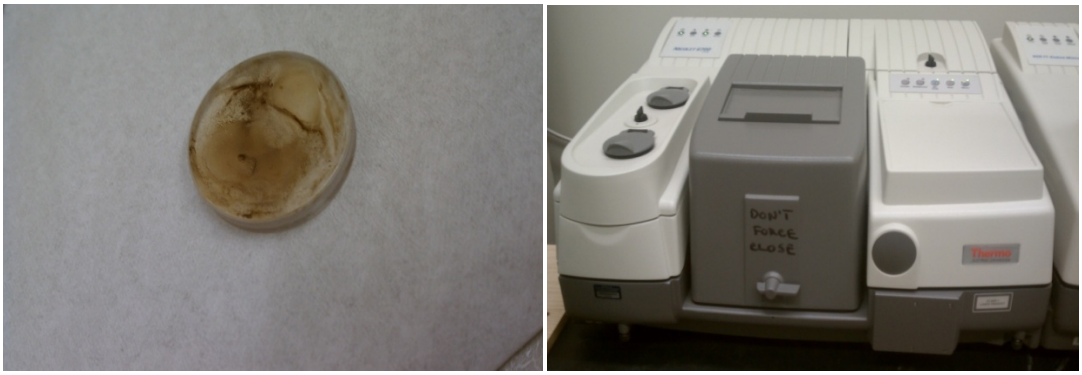
Two divynlbenzene multi-pore GPC columns are used in the TOSOH EcoSEC GPC. A guard column is also inserted to prevent any clogging in the multi-pore columns. The EcoSEC GPC requires the solvent tetrahydrofuran (THF) for its mobile phase. THF is also a strong solvent for asphalt. Recovered asphalt is carefully massed, then THF is added to create a solution of specified concentration; in this study the concentration is 1 mg of asphalt per 1 mL of solvent.

Each sample is then filtered through a 0.2μm filter into an auto-sample vial, and the cap is secured. Each auto-sample vial is then placed into the GPC's auto-sampler. The sample is then activated through the software provided with the EcoSEC GPC. Each specimen required approximately 15 minutes to complete.

3.3.5 Fourier Transform Infrared Spectroscopy

Toluene, another common asphalt solvent, was added to the recovered asphalt binder. The binder was then drop cast onto a potassium bromide (KBr) salt plate. The solvent is then allowed to evaporate from the solution, leaving a thin film, as seen in Figure 3.1.

After the solvent has evaporated, the salt plate is placed into a vacuum oven at 80°C over night to ensure all solvent has been evaporated.



(a.) (b.)

Figure 3.1 (a.) Asphalt film drop cast on KBr salt plate. (b.) Nicolet FTIR

The KBr plate is removed from the vacuum oven and allowed to cool. Then the plate is placed vertically in the FTIR and the spectra was collected. The Nicolet software is then used to evaluate the spectra. A background spectrum for the KBr plate should be recorded by the FTIR prior to drop casting the specimen.

3.4 Results and Discussion

3.4.1 Virgin Mixture GPC Evaluation

To evaluate the methodology of staged extraction and whether chemical constituents were equally extracted as opposed to selectively extracted the LMS percentage was studied for the virgin mixture. Due to its minimal oxidation exposure, the virgin mixture

should have the least variation in binder stiffness between layers and therefore the LMS percentage should be relatively consistent throughout. The chromatogram is evaluated between ~8.5 minutes and ~11.75 minutes, which is the range in which the asphalt molecules began to elute. A summation of the area beneath the chromatogram for the first 5 slices was computed. The absorbance of the RI detector, as shown in Figure 3.2, will vary. This is attributed to a slight concentration change in each asphalt solution or minor changes in response due to testing on different days. The absorbance signifies a detection of the amount of material that elutes, if there is a higher concentration and therefore an increased number of molecules in the solution, more molecules will be detected. Thus it is important to normalize the curves, which taking a ratio with respect to total area will accomplish.

When the virgin mixture was evaluated using staged extraction and GPC it was found that percent LMS was within 0.83% for all four layers. The uniformity of each layer shows that the asphalt binder is uniformly being extracted from the mixture. A duplicate sample was tested to evaluate repeatability and a maximum coefficient of variability (CV), or standard deviation divided by the mean expressed as a percentage, is 8.28%. Thus any concern about whether the TCE is extracting certain components of the asphalt binder before others is dismissed. The comparative chromatogram is provided in Figure 3.2.

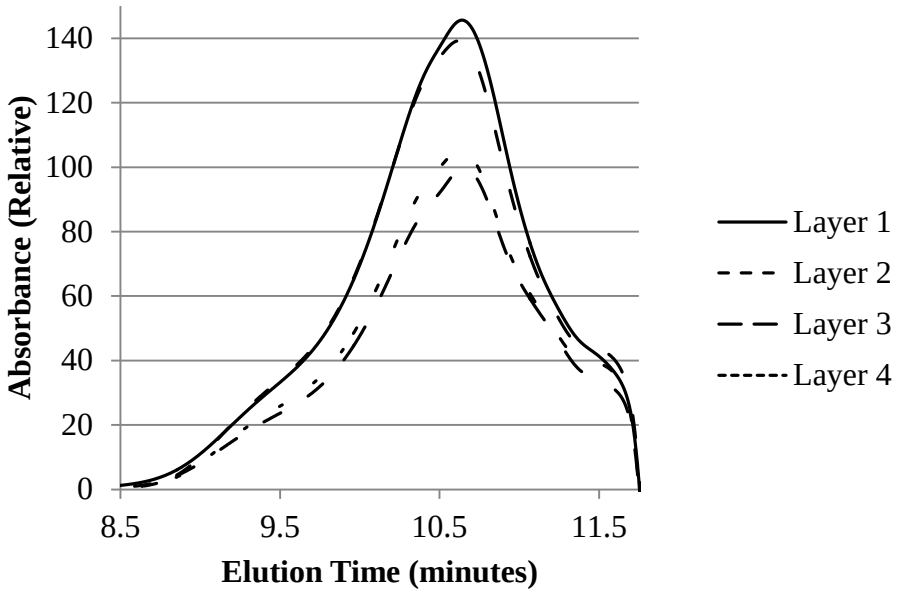


Figure 3.2 Virgin mixture extraction.

3.4.2 RAP and RAP Blend GPC Evaluation

The RAP and RAP blend were evaluated along with the virgin mixture along the same elution time interval. The dipping time for each layer of the virgin mixture was only 30 seconds due to the increased speed of extraction for an un-aged binder. The RAP and RAP blend were evaluated at dip increments of 30 seconds and 1 minute (i.e. 1 minute is equivalent to 1 minute of dipping per beaker of fresh TCE, totaling 4 minutes for the total extraction). An additional 3 minute dip increment was studied for the RAP.

The LMS percentage for RAP was significantly higher than that of the virgin mixture. The mean value over all layers of RAP was 12.24% LMS as compared to the mean value of the virgin mixture LMS of 6.13%. This is to be expected considering the RAP has

been significantly aged resulting in a stiffer binder. The data revealed that there was little variation between all layers. The greatest differentiation between RAP was 1.24% between layers 2 and 4 of the 30 second wash. The maximum coefficient of variability for the 30 second RAP wash is 6.59% and the maximum CV for the 1 minute RAP wash is 13.28%. It is of no surprise that a higher CV value is found in comparison to the virgin mixture because RAP is going to have very different oxidation characteristics due to the complex factors in which RAP oxidation occurs.

For analyzing the RAP blend only the RAP aggregate were removed for testing. This is because it was known that the RAP had come into contact with the virgin binder, thus if blending occurs between the virgin and RAP binder it would be detectable. If blending had not occurred, yet all aggregate was subject to testing, the results of the staged extraction would have been skewed and inaccurate. The blend tests revealed LMS values between approximately 7.5% and 9%, with a mean value of 8.54%. When examining the average of the virgin mean and RAP mean of 9.34%, an average blend value of 8.51% would imply that blending is occurring. All blended data is available in Figure 3.3 and Figure 3.4. Duplicate tests were performed to investigate the variability within the blended mixture. A maximum CV of 5.91% was found for the 30 second wash increment and 5.14% was found in the 1 minute wash increment. Figure 3.5 is indicative of the GPC findings in its comparison of layer 2 of the virgin mixture, RAP blend, and RAP after 30 second staged extraction.

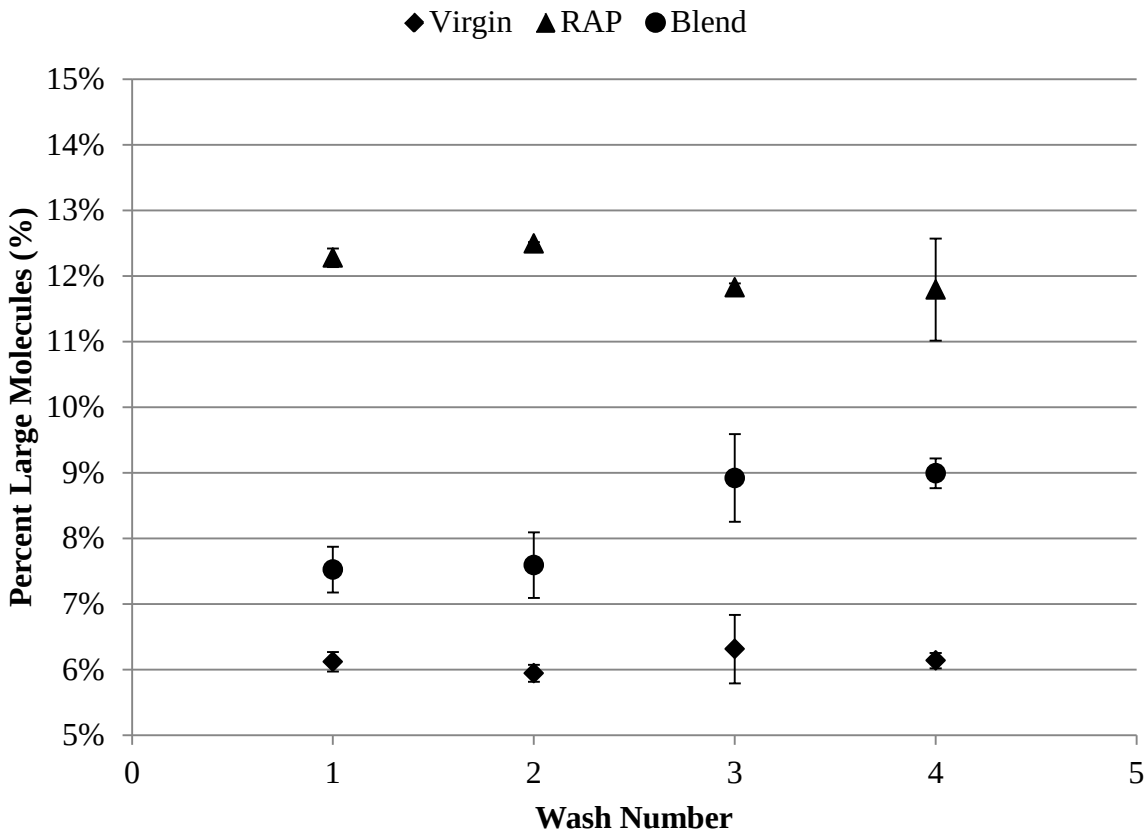


Figure 3.3 Comparison of Virgin, RAP, and blended mixtures with 30 second washes

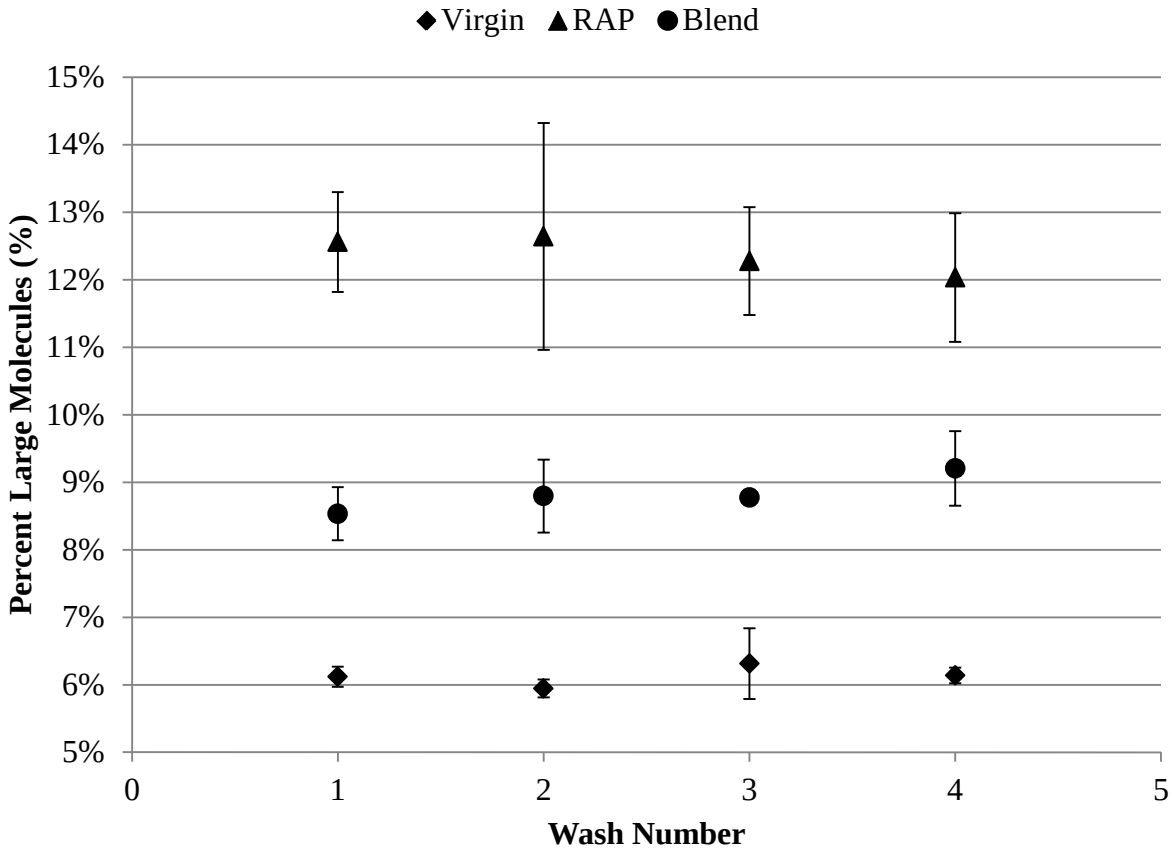


Figure 3.4 Comparison of Virgin, RAP, and blended mixtures with 1 minute washes (Virgin mixture 30 second washes)

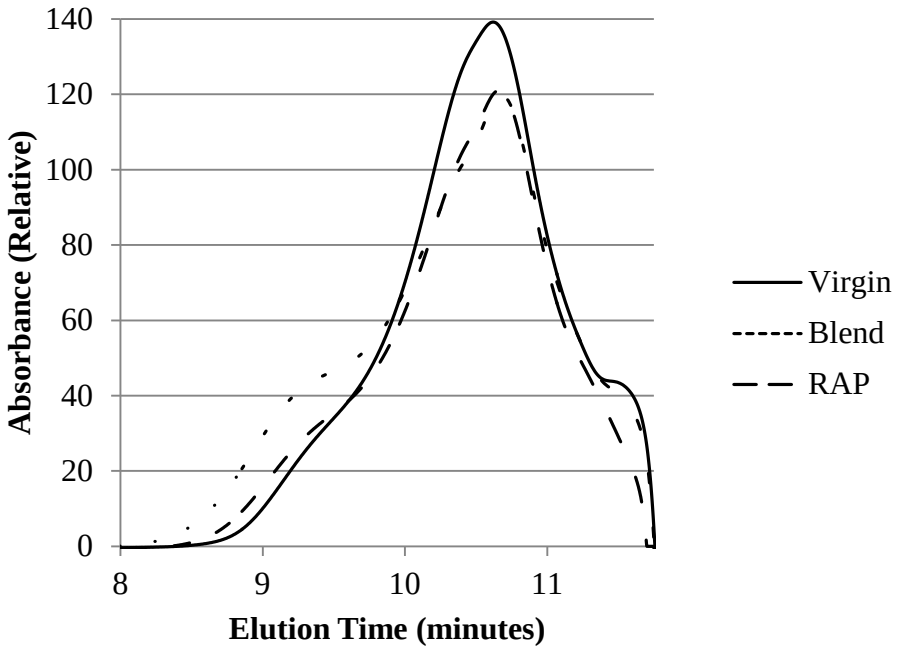


Figure 3.5 Comparison of layer 2 of Virgin, Virgin-RAP blend, and RAP

The 30 second extraction of the RAP blend shown in Figure 3.3 reveals a notable result. As each layer is removed, the percentage of LMS increases. This would imply that the outermost layer, while still between the virgin and RAP binder LMS is more similar to the virgin asphalt binder than the RAP asphalt binder. As each layer is removed, the LMS% increases, until the final layer removed is closer to that of the RAP asphalt binder than of the virgin binder. Thus a system is formed where the binder stiffens closer to the aggregate. It is important to note that the binder does not ever reach an LMS% of the RAP, and thus a "black rock" phenomenon is not exhibited. The 1 minute extraction of the blended mixture reveals very similar data with respect to the mean values. There is an initial increase in the LMS% as compared to the 30 second extraction is to be expected because the first layer of the blended mixture is extracted twice as long, thus causing the mean stiffness of the layer to increase. Layers 2 and 3 are 0.03% apart, and though the

second layer has a higher LMS than the third layer, the difference is considered to be negligible. The final layer is higher in LMS% than all other layers indicating increased stiffness in accordance to the research conducted by Kim et al (2006).

3.4.3 FTIR Evaluation of Artificial RAP Blend

A ratio of the carbonyls (C=O) was taken in comparison to the saturated C-C vibrations to evaluate oxidation. This ratio is presented in Figure 3.7 as the carbonyl (%) and defined by taking the area beneath the C=O and C-C peaks, A1695/A1455. An increase in the carbonyl is characteristic of an increase in the oxidation, or aging, of the asphalt binder. An example of how these areas are calculated is given in Figure 3.6.

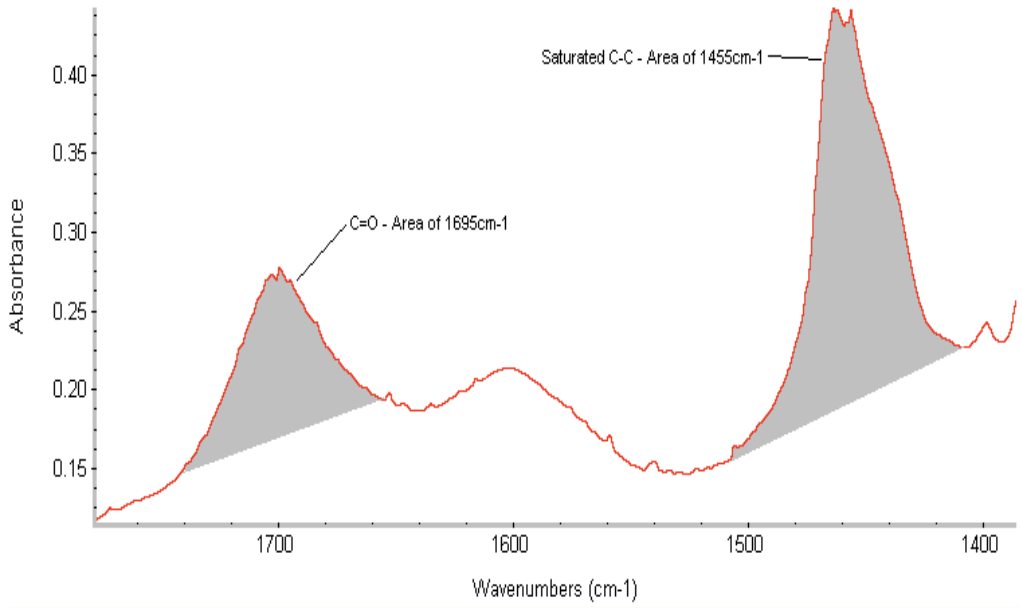


Figure 3.6 Area of carbonyl versus area of saturated C-C in FTIR spectra

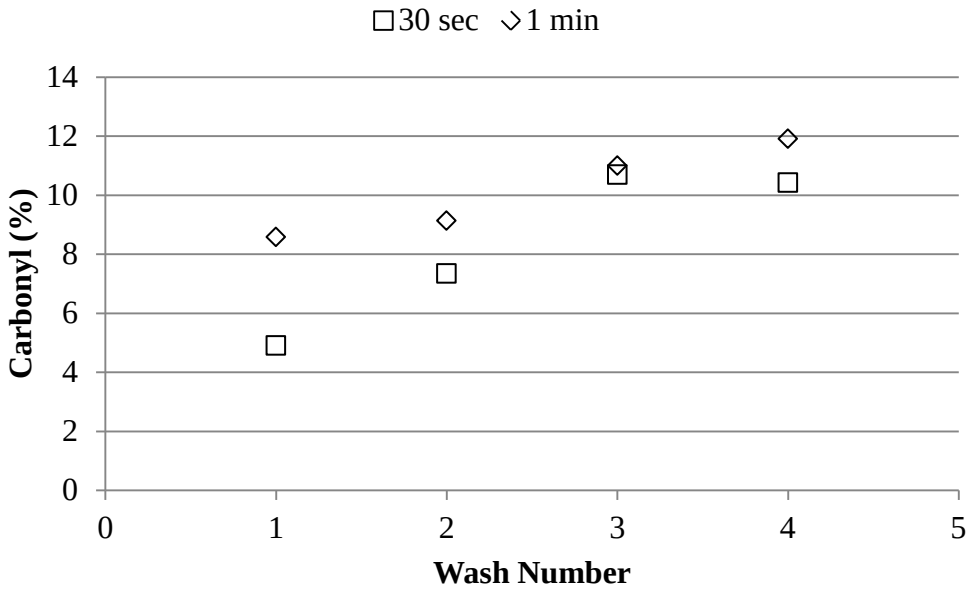


Figure 3.7 FTIR evaluation of carbonyl increase in blend with artificial RAP

The evaluation of the carbonyl band in each layer of the artificial RAP blend found similar results to that of the GPC. Virgin PG64-22 asphalt collected from the same source and batch of asphalt as used for the artificial RAP and blended asphalt yielded a carbonyl ratio of 2.09% and can be used as a base for comparison of oxidation as aging occurs for this batch of asphalt cement. In all phases of experimental extraction time, the outermost layer exhibits less oxidation than that of the inner layers of the blend.

In the 30 second extraction oxidation of outermost layer is 4.91%. The inner most layer is 10.43%, nearly 6% higher in carbonyl presence. The outermost layer is higher than that of the virgin PG64 by a difference of greater than 2%, which is attributed to the oxidation that occurred during the mixing process as well as some potential blending between the virgin asphalt and the artificial RAP asphalt. The virgin binder tested to establish this 2%

difference was the same binder source as used in the mixtures; however it was tested by simply adding toluene and drop casting to the KBr salt plate for evaluation. The ratio of carbonyl presence increases steadily as the virgin binder penetrated the artificial RAP binder.

The 1 minute extraction yielded values that are expected from a blended mix with RAP. The outermost layer of asphalt is approximately 2.5% lower than that of the innermost layer. Each layer has an increase of carbonyl presence as you move toward the aggregate. This indicates that the virgin asphalt penetrates the RAP, but it was not able to completely blend uniformly. The higher value of carbonyl for the inner most layer of the 1 minute extraction set as compared to the 30 second extraction set is attributed to the fact that the inner most layer of the 30 second extraction contains asphalt which is further from the aggregate, which has shown to be softer.

3.4.4 Artificial RAP Blend GPC Evaluation

Testing of a blend using laboratory prepared artificial RAP yielded similar results as that of the blend with true RAP. Percentages of large molecules range between 5.70% and 6.95% in both samples. The data yielded a linear trend, revealing in an increase of large molecules in layers closer to the RAP aggregate. This trend was most readily identified in the 1 minute dip time increment for the artificial RAP blend. The collected data is shown in Figure 3.8.

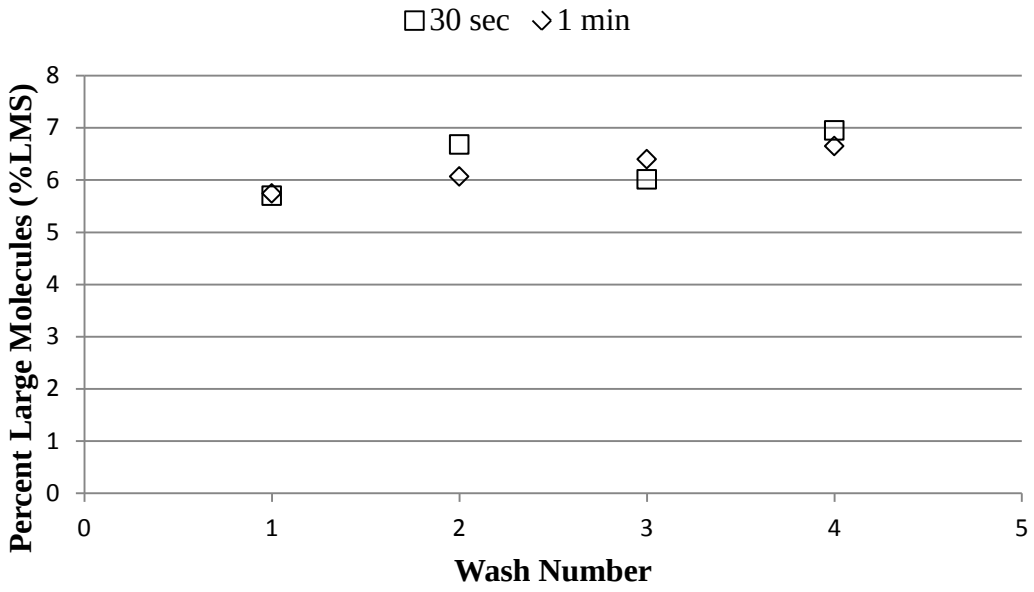


Figure 3.8 Percent of large molecules in artificial RAP blend

A comparison of the results of the FTIR and the GPC test on the same artificial RAP blend samples yields very similar results. In both testing cases it was found that the blend does not occur uniformly throughout the mixture, but that there in a general increase in the penetration of the virgin asphalt binder into the artificial RAP binder as each layer gets closer to the aggregate. More importantly however is the difference in the percentage values found between the tests. The GPC yielded a difference of 1.25% between the outermost layer and innermost layer while FTIR yielded a difference of 7.00% for the same samples. Based on this analysis, it seems that the FTIR gives a more accurate depiction of the differentiation in the aging of the asphalt binder layers.

3.5 Conclusions

A study has been conducted to evaluate the blending efficiency of RAP within an asphalt pavement mixture by the staged extraction method. The extracted asphalt binder was tested using two chemical testing techniques, Gel Permeation Chromatography and Fourier Infrared Transform Spectroscopy. The results of these tests yield the following conclusions:

- Based on the GPC results of the virgin mixture the staged extraction is a viable method to be used to evaluate different layers within an asphalt mixture.
- GPC and FTIR can be used to analyze the aging characteristics of the binder layers within the asphalt mixture.
- GPC testing found that blending does occur within all layers of the pavement mixture, but the blending is not completely uniform.
- FTIR testing found that blending occurred in all layers of the mixture, but the blending is not completely uniform.
- Based on a comparison of tests between the same materials the FTIR yielded a higher differentiation in ratio than the GPC. This leads to the belief that the FTIR may be more effective for determining asphalt aging properties in a layered system. However, the RAP needs to be considered when using FTIR because the C-C stretch peak used for normalization may not remain constant between asphalt binders of different grade or from different sources.

- It is recommended that staged extraction be performed on asphalt mixtures at a 1 minute dip time as compared to 30 seconds for similar asphalt mixtures as described in this study.

3.6 Acknowledgement:

The authors would like to thank the financial support of the Tennessee Department of Transportation (TDOT) and the Federal Highway Administration (FHWA). The views expressed within this manuscript are those of the authors and do not necessarily represent the views of TDOT and FHWA.

CHAPTER IV

BLENDING EFFICIENCY OF RECLAIMED ASPHALT PAVEMENT: AN APPROACH UTILIZING RHEOLOGICAL PROPERTIES AND MOLECULAR WEIGHT DISTRIBUTIONS

A version of this chapter will be submitted for publication by Benjamin F. Bowers, Jason Moore, Baoshan Huang, and Xiang Shu:

Bowers, B.F., Moore, J., Huang, B., and Shu, X. "Blending Efficiency of Reclaimed Asphalt Pavement: An Approach Utilizing Rheological Properties and Molecular Weight Distributions".

Benjamin F. Bowers was the principle researcher and author of Blending Efficiency of Reclaimed Asphalt Pavement: An Approach Utilizing Rheological Properties and Molecular Weight Distributions". Benjamin's contribution was conducting all literature review, testing, data analysis, and writing the text contained in the manuscript. Dr. Baoshan Huang and Dr. Xiang Shu provided guidance and ideas throughout the research process as well as editorial assistance. Jason Moore worked with Benjamin to create all mixtures and recover the binder, as well as with some rheological testing.

4.1 Abstract

Different mixing conditions are expected to have a large influence on the ability for Reclaimed Asphalt Pavement (RAP) and virgin binder to blend in an asphalt pavement mixture. This study investigates the influence of mixing time, mixing temperature, and the inclusion of Warm Mix Asphalt (WMA) additives on the ability to RAP and virgin binder to blend. A large virgin aggregate and a small RAP were blended with virgin binder in defined mixing scenarios. The aggregates were then separated and the binder was recovered and the rheological and chemical properties were investigating using the Dynamic Shear Rheometer (DSR) and Gel Permeation Chromatography (GPC). This research found that there is a limit to which mixing time has an influence on binder blending, mixing temperature has a significant effect, and the inclusion of WMA additives has a positive effect on blending.

4.2 Introduction

4.2.1 Blending Efficiency

In efforts to reuse asphalt binder and conserve natural resources there is high interest from both industry and academia in the blending efficiency of Reclaimed Asphalt Pavement (RAP) in new pavement mixtures. The asphalt binder in RAP is generally much stiffer than that of a new, virgin binder. This is due to the oxidation that occurs within the binder caused by the thermal effects during the mixing process and the environmental effects during the pavements life cycle. When the RAP is recycled into the new pavement mixture, the assumption is made that the RAP binder is blending with the new virgin binder. This assumption is critical in considering the long term performance of the new pavement mixture. If the stiff RAP binder does not blend with the virgin binder, the pavement performance could be compromised. At higher percentages of RAP (>15%) the virgin binder grade is often decreased in order to account for the increased stiffness of the mixture due to the RAP binder (Khandal and Foo 1997). This creates an even more complicated problem if the binders are not efficiently blending because there will potentially be pockets of stiff, RAP binder and virgin binder which is too soft for the climactic region. Thus it is very important to establish the efficiency of the blend in order to properly engineer the pavement to serve its entire expected life span.

Many studies have been conducted to investigate the blending efficiency of RAP in asphalt paving mixtures. Soleymani et al. (2000) investigated blending efficiency by

creating three very different mixes for comparison. One applied theory is that the RAP simply acts as a “black rock”, meaning that the RAP binder does not blend at all with the new virgin binder. Soleymani et al. created three mixtures, Case A, B, and C, at 10 and 40% RAP content. Case A is the “black rock” scenario where the RAP binder was recovered from the RAP aggregate and only the RAP aggregate was used in the mixture. Case B is a “true” mixing scenario where the RAP is simply added to the mixture as it would be in typical mixing cases. Case C is the considered the “total blend” scenario because the recovered RAP binder from Case A was blended mechanically with the virgin binder before adding it to the mixture. All three mixtures were then tested using the Simple Shear Tester (SST). After testing over 64 cases, it was found that for 40% RAP content, 45% of the samples performed similar to the Case C, 100% blend. Only 5% of the mixtures performed close to the “black rock” scenario, and the remaining samples were somewhere in between in terms of performance. At 10% RAP content, little to no difference was detectable between Case A, B, and C.

McDaniel et al. (2012) conducted a study that examined field mixtures with different RAP contents and similar gradations, and then defined their blending based on the “Bonaquest Approach”. This approach takes into consideration the fully recovered binder from a mixture. In the case of a full recovery on a mixture, the binder is considered to be completely blended. The recovered binder was tested using the dynamic shear rheometer (DSR) and the bending beam rheometer (BBR). The Hirsch Model was applied to estimate the mix master curve. The mixtures were then tested and compared to the

predicted master curve. If the master curves overlapped, the mixture was considered to be a total blend. Twenty-four mixtures were considered with RAP contents ranging between 0%-40% and two different performance grade virgin binders. Three of the mixtures that included RAP were considered to exhibit poor blending, one had partial blending, and the remaining 16 mixtures were considered to be well blended. Mogawer et al. (2012) used a similar method to investigate the blending efficiency of plant-produced mixtures. The Christenson-Anderson model was used to develop the mixture master curve. An important finding of this research is that the discharge temperature may have an impact on the relative degree of blending.

Additional studies to evaluate blending efficiency were conducted by Huang et al. (2005a) and Bowers et al. (2014a). In both studies a mixture was created with two different sized materials. A virgin binder was mixed with large virgin aggregate and a smaller RAP. After mixing, the large aggregate and small aggregate were separated. The small (RAP) aggregate was then subjected to a "staged extraction" method where the aggregate was washed four times with solvent, removing "layers" of binder. In the study conducted by Huang et al. the binder was recovered and characterized using the DSR and Finite Element Analysis. Huang et al. found that a composite layer was formed between the virgin and RAP binders, but effectively a three layer system was formed with the innermost layer being more stiff. Bowers et al. (2014a) also recovered the binder, but then tested it using the analytical chemistry techniques Gel Permeation Chromatography (GPC) and Fourier Transform Infrared Spectroscopy (FTIR). In the work of Bowers et al.

it was determined that a partial blend occurred in all four layers, with the outermost layer being the softest and gradually stiffening when moving to the innermost layer.

Zhao et al. (2013a) investigated the blending efficiency of Recycled Asphalt Shingles (RAS) using DSR and GPC. Three different sized aggregates were used in this study and separated after mixing. The fine particles were blended with the RAS prior to mixing with a medium and large aggregate. Mixing scenarios varied in this research from different mixing time and different mixing temperature. The researchers concluded that aggregate size and mixing temperature did not play a role in the blending efficiency of the RAS, but they did identify an effect of the mixing time. Also worth noting is that the RAS never completely blended with the virgin binder. Navaro et al (2012) studied the blending of RAP microscopically by using a virgin binder that is clear under white light but has polymers that fluoresce under UV light. The researchers created mixtures at 110°C, 130°C, and 160°C. The mixtures were then examined microscopically and the researchers determined that at higher mixing temperatures the RAP particles were less likely to cluster, implying that better blending occurs at higher temperatures. Shirodkar et al. (2011) conducted a study with large virgin aggregates and small RAP aggregates. The researchers superheated the virgin aggregates and then added the RAP aggregates for 30 minutes prior to mixing. The RAP was then mixed with the virgin aggregates and placed back in the oven for 2.5 hours. The mass loss from the RAP was then calculated and was considered to be the amount of binder that could mobilize. At the conclusion of the research, it was found that 70% blending occurs in a 25% RAP content with a PG70-28.

The researchers also found that up to 96% blending occurs when 35% RAP is blended with a PG58-28 binder. Both findings were based on the authors given gradation.

The use of Warm Mix Asphalt (WMA) will allow for asphalt mixtures to be created at temperatures between 10-38°C lower than traditional HMA temperatures. This provides economic and environmental benefits. The use of WMA additionally limits the susceptibility of binder to oxidation during the mixing process. Zhao et al. (2013) investigated the use of foamed asphalt and the surfactant based product, Evotherm, with high RAP contents ranging from 0% to 40% and compared the rut resistance, fatigue resistance, and moisture susceptibility. Shu et al. (2012) investigated the impact of RAP in both HMA and WMA mixtures and found that RAP is beneficial for resistance to moisture damage. Further work studying the combination of WMA and RAP by Zhao et al. (2012) found that foamed WMA actually had better resistance to rutting, moisture damage, and fatigue performance when compared to HMA equivalents. There are obviously economic and environmental benefits to the use of RAP and WMA together; however the question still remains on how WMA may affect the blending efficiency of RAP consider the lower temperatures.

4.3 Objective

The objective of this study is to investigate the effects of mixing temperature, mixing time, and the inclusion of WMA additives on the blending efficiency of RAP binder in

asphalt paving. The rheological and molecular properties are investigated to help determine the amount of blending that is occurring as the mixing conditions change.

4.4 Materials and Methods

4.4.1 Materials

Materials used in the mixture were Performance Grade (PG) 64-22, RAP of an unknown source, and a virgin aggregate. The RAP was processed by first barrel rolling two minutes and then sieved eight minutes, collecting only material retained on the #4 and #8 sieves. The process was for assurance of no agglomerates and minimizing dust. An extraction and recovery of the processed RAP was performed with a resulting asphalt content of 3.24%.

The virgin aggregate was sieved and the material retained on the 1/2-inch sieve was collected. The sizes were chosen based on the ability to readily distinguish the two materials after mixing with the virgin binder. A total asphalt binder content of 3.00 percent was selected with a rap binder replacement of 2.10 percent. The percentages were selected based upon trial blending and recovery testing. Additionally, based on preliminary trials, it appeared that the smaller aggregate size of the RAP had a great percentage of coating due to increased surface area. The percentages of RAP, virgin binder and RAP binder replacement for the mix were selected for assurance of total

virgin binder coating on the smaller RAP aggregates did not saturate the RAP to an unrealistic level and reduce the margin of the ability to distinguish virgin binder from RAP binder. The surfactant based WMA additive Evotherm and the wax based WMA additive Sasobit were additionally studied. Both additives were added to the PG64-22 binder for their respective mixtures.

4.4.2 Mixing Methodology

The virgin binder was heated to mixing temperatures on the basis of the test matrix (Table 4.1) and the virgin aggregate was superheated to 10°C beyond the mixing temperature. The RAP was not heated so that any blending was induced by the superheated aggregates, which is similar to the processes that occur in the asphalt plant.

In efforts to ensure that the virgin binder coated the coarse aggregate, the aggregate and binder were mixed for one minute prior to the addition of RAP. The RAP was then added and allowed to mix for the duration of mixing time provided in the experimental matrix (Table 4.1). This step was important because the RAP aggregates are smaller in size. The virgin binder was found to have a tendency to coat the smaller aggregates first. This caused a larger portion of virgin asphalt to coat the RAP without coating the larger, leaving very little virgin asphalt to coat virgin aggregates. A Hobart Mixer model A-120 with wire whisk was used for mixing.

Table 4.1 Experimental matrix of mixing scenarios

Mixture	Additive	Time (s)	Temperature (°C)
1	-	30	160
2	-	60	160
3	-	105	160
4	-	150	160
5	-	300	160
6	-	105	130
7	-	105	180
8	Evotherm	105	130
9	Sasobit	105	130

At the conclusion of mixing, the large, “coarse” (virgin) and small, “fine” (RAP) aggregates were separated. Upon separation, the binder was recovered from the mixtures using AASHTO T164 “Standard Method of Test for Quantitative Extraction of Asphalt Binder from Hot-Mix Asphalt (HMA)”. The solvent used for the extraction and recovery was n-propyl bromide.

4.4.3 Master Curve Generation

The recovered binder was used for the generation of a master curve for both the coarse and fine aggregates of each mixture. An Anton Parr Dynamic Shear Rheometer (DSR) was used to generate the master curves. The test temperatures were 10°C, 25°C, and 40°C with a frequency range of 0.01, 0.1, 1, 10, and 25 Hz. An 8 mm. DSR plate was used for testing.

4.4.4 Gel Permeation Chromatography

Asphalt has been characterized with Gel Permeation Chromatography (GPC) for many years. Many studies have been conducted in efforts to connect the GPC outputs to the performance properties commonly considered in the characterization of asphalt binders. The GPC provides a molecular weight distribution of a given medium, in this case asphalt cement. This molecular weight distribution can be separated into three different major fractions, Large Molecular Sizes (LMS), Medium Molecular Sizes (MMS), and Small Molecular Sizes (SMS). The current research practices have not found a correlation between asphalt binder performance properties and the MMS and SMS. However, many works have found a relationship between the LMS and different performance properties of asphalt binders. Zhao et al. (2013a) correlated the LMS of recycled asphalt shingles (RAS) to the complex modulus (G*) of the asphalt binder at 25°C and 64°C. This research was performed by mechanically mixing recovered RAS binder with virgin asphalt binder. Kim et al. (2006) correlated the increase in LMS% to an increase in RAP binder viscosity. LMS% is defined by the area beneath the chromatogram. When dividing the chromatogram into 13 slices the first 5 are considered the LMS. The LMS% equation is provided in equation 4.1 (Doh, Amirkhanian, and Kim 2008, Lee, Amirkhanian, and Shatanawi 2006, Kim et al. 2006, Bowers et al. 2014, Zhao et al. 2013a):

$$\text{LMS\%} = \frac{\text{Area of first } \frac{5}{13} \text{ of chromatogram}}{\text{Total Area beneath chromatogram}} \text{x } 100 \qquad (4.1)$$

A TOSOH EcoSEC GPC was used for analyzing the recovered binder from the coarse and fine particles of each mixture. The packing material for the GPC column was a polystyrene divinylbenzene copolymer. The elution solvent used was tetrahydrofuran (THF).

4.5 Results and Analysis

4.5.1 Effect of mixing time

The recovered binders from the coarse and fine aggregates were tested for their rheological properties. In a poor mixing condition, the fine (RAP) aggregate is expected to exhibit stiff rheological properties due to the presence of the RAP binder, while the coarse aggregate is expected to exhibit soft rheological properties since it was mixed with virgin binder prior to RAP inclusion. The rheological master curve results for the different mixing times can be found in Figure 4.1.

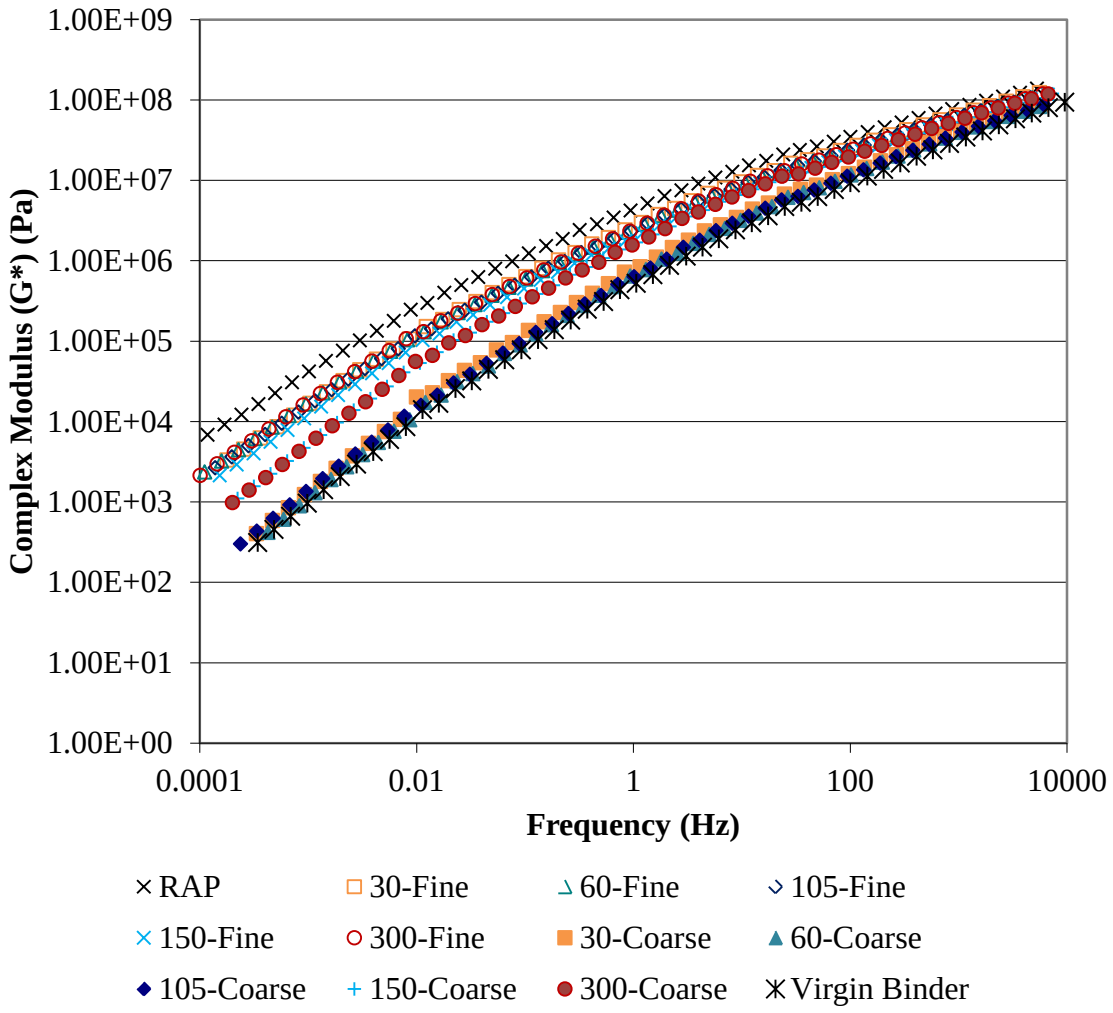


Figure 4.1 Master curve of the Complex Modulus (G*) for changing mix times

The master curve data shows that there is a large gap between the virgin binder and RAP binder curves. In the case of the virgin binder curve, the binder was recovered from a coarse mixture that contained no RAP. At 30, 60, and 105 seconds, there is no noticeable differentiation between the coarse master curves. However, when the mixing time reaches 150 seconds there is an evident increase in the complex modulus at the lower

frequencies. This indicates that there is an increase in the presence of RAP binder in the binder recovered from the coarse aggregate.

A ratio for the LMS% of the coarse aggregate to the fine aggregate was considered for an estimation of the efficiency of blending. The RAP binder exhibits a significantly higher LMS% than virgin binder. Thus, if RAP binder blends with the virgin binder on the coarse, virgin aggregate, the LMS% should increase. Likewise, as the virgin binder blends or diffuses into the RAP binder on the fine aggregate, the LMS of the fine aggregate should decrease. If the LMS% for the binder recovered from the coarse aggregate, which has been increasing in the number of large molecules present, is equivalent to that of the binder recovered from the fine aggregate which is decreasing in large molecules as the virgin binder blends and/or diffuses into the RAP binder, then a complete blend will have been achieved. The blending ratio is computed as follows:

$$\text{Blending ratio} = \frac{\text{Coarse LMS\%}}{\text{Fine LMS\%}} \tag{4.2}$$

At a typical mixing temperature of 160°C the times were increased from 30 seconds to 150 seconds, as shown in Table 4.1. The blending ratio gradually increased from just over 55% at 30 seconds of blending to nearly 80% after 150 seconds. This data is plotted and projected as shown in Figure 4.2, to estimate the total time, assuming linearity, to achieve a 100% blend. A linear regression was performed on the data, which yielded the following equation 4.3 for the estimation of the blending percentage with respect to time:

$$\text{Blending Ratio} = 0.1591(\text{Seconds of Mixing}) + 49.73 \quad (4.3)$$

On the basis of the regression equation, it would take over 5 minutes to achieve a 100% blend. That is not a realistic time frame for mixing in a practical field application. A 5 minute mixing time was attempted, as shown in Figure 4.2. The solid square data point represents the blend ratio for the 5 minute mixing time case.

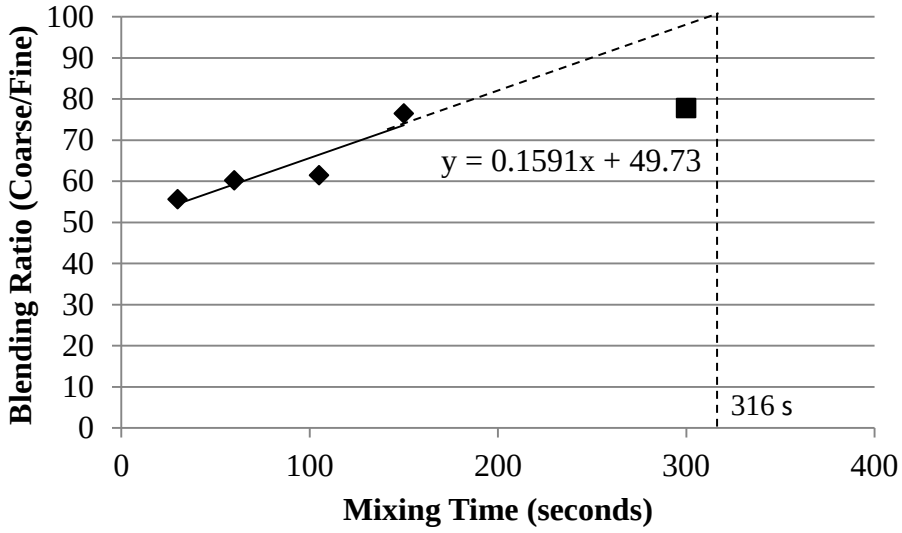


Figure 4.2 Regression of 30, 60, 105, and 150 second blending ratio results to calculate 100% blend ratio. Blending ratio at 300 seconds is also presented (Solid Square)

An important finding as noted in Figure 4.2 is that doubling the mix time beyond 150 seconds to 300 seconds only achieved a one percent increase in blend ratio from 77% to 78%. In this mixing scenario it can be concluded that an increase in mixing time is not helpful in creating an increase in blend ratio, and the trend is not linear beyond 150 seconds. This is believed to be largely due to the lack of continuous heating throughout the mixing process.

4.5.2 Effect of mixing temperature

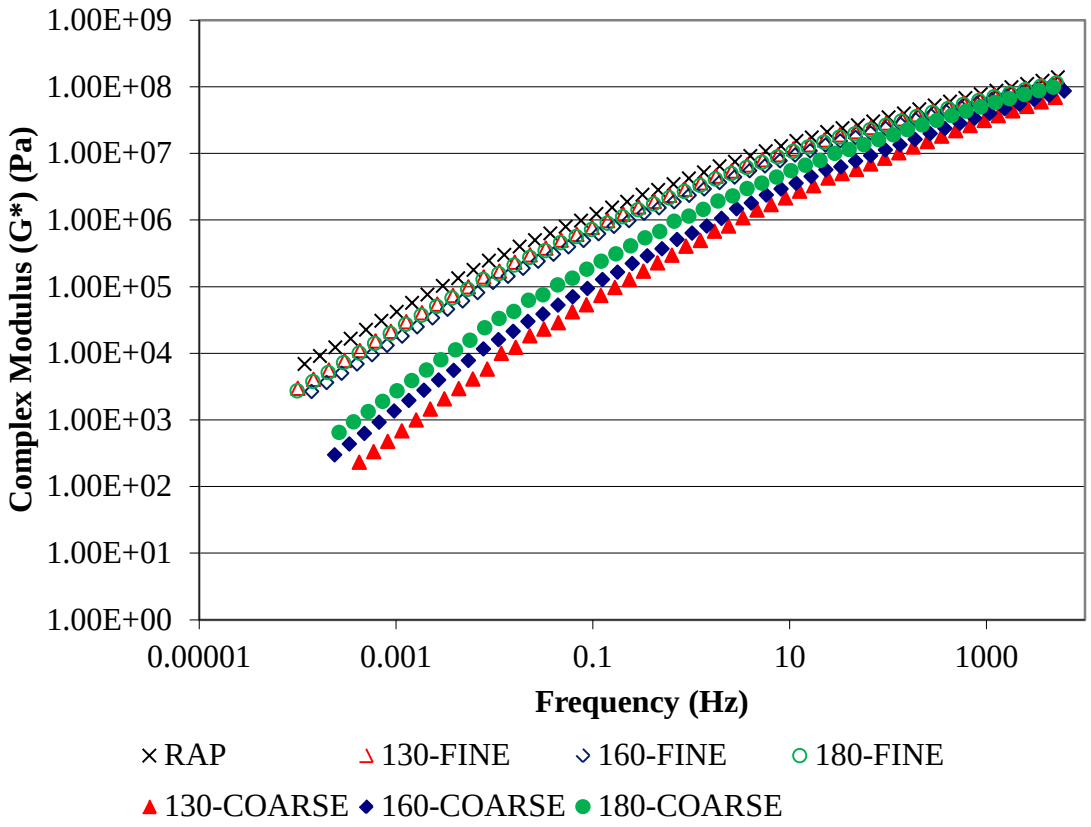


Figure 4.3 Master curve of the Complex Modulus (G*) for changing temperatures

The master curve shown in Figure 4.3 reveals the influence of mixing temperature on the blending of the binders. The coarse aggregate clearly increases in complex modulus as the mixing temperature increases from 130°C to 160°C and from 160°C to 180°C. Furthermore the fine aggregate master curves never have any clear separation, indicating that the fine aggregate, originally coated in RAP binder, is not further oxidized even at higher temperatures. This is further supported when examining Figure 4.4 which shows the average LMS% and standard deviation for both the recovered fine and coarse binders.

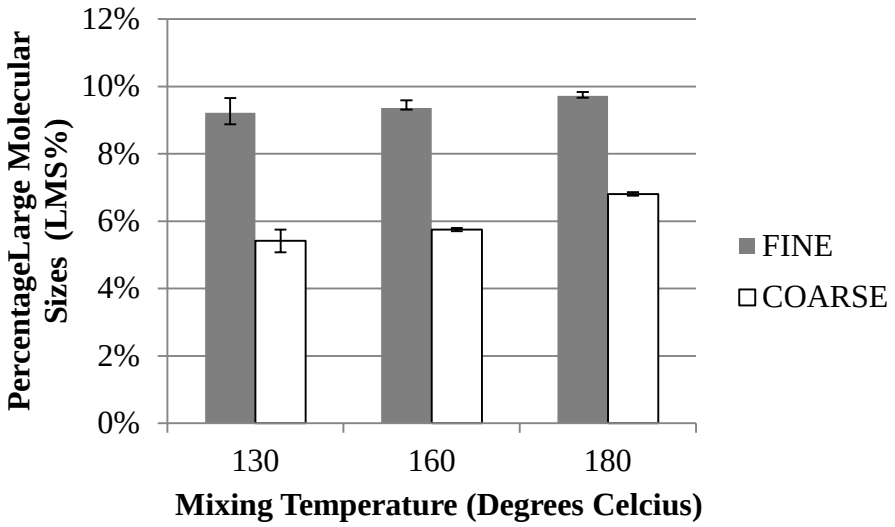


Figure 4.4 Course and fine LMS% at varying temperatures at a 105 second mix time

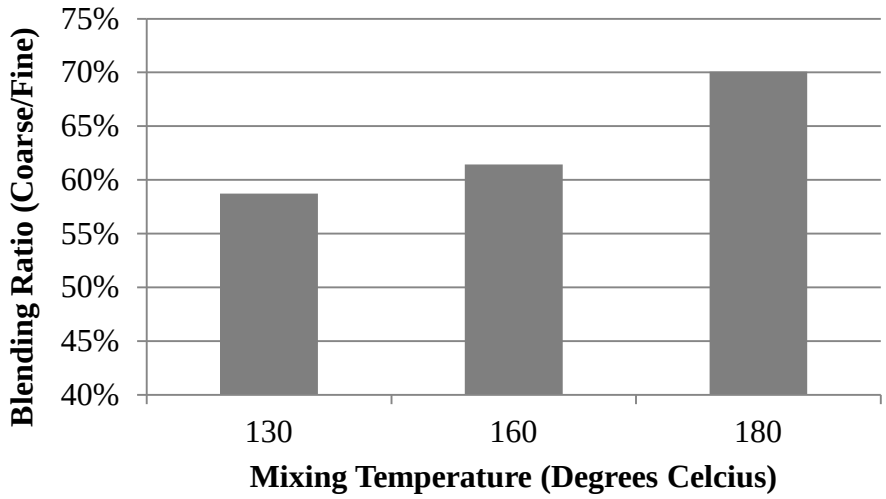


Figure 4.5 Blending Ratio for varying mix temperatures at a 105 second mix time

The data presented in Figure 4.5 shows that there is an increase in blending ratio as the mixing temperature increases. This is to be expected, however there it should be noted that since there is no increase in the LMS% for the fine aggregate, it is clear that the binder on the coarse aggregate is indeed receiving some of the effective RAP binder. This

is likely because the hot virgin aggregates and the hot virgin binder can assist in melting the RAP binder, allowing for further diffusion of the two binders into one another.

4.5.3 Effect of Warm Mix additives

The evaluation of WMA additives compared to a control mixture yielded interesting results. In both cases, the WMA additive showed to increase the blending ratio. However, as seen both by the master curve in Figure 4.6 and the blending ratio in Figure 4.7 the Evotherm WMA additive induced better blending than either the Sasobit mixture or the control mixture. The Evotherm mixture had a blending ratio equivalent to that of the 160°C, 150 second mixture even though it was mixed for less time and at a lower temperature. This indicates that Evotherm actually does assist in the blending of RAP and virgin binders. The researchers did notice that Sasobit seemed to increase the workability and more easily coated the RAP when the coarse aggregates with virgin binder were mixed together. Further investigation into the use of Sasobit at a longer mix time (150 seconds) or a higher temperature (160°C) may be worth investigating to see if these two variables play a significant impact in Sasobit's ability to increase RAP blending efficiency.

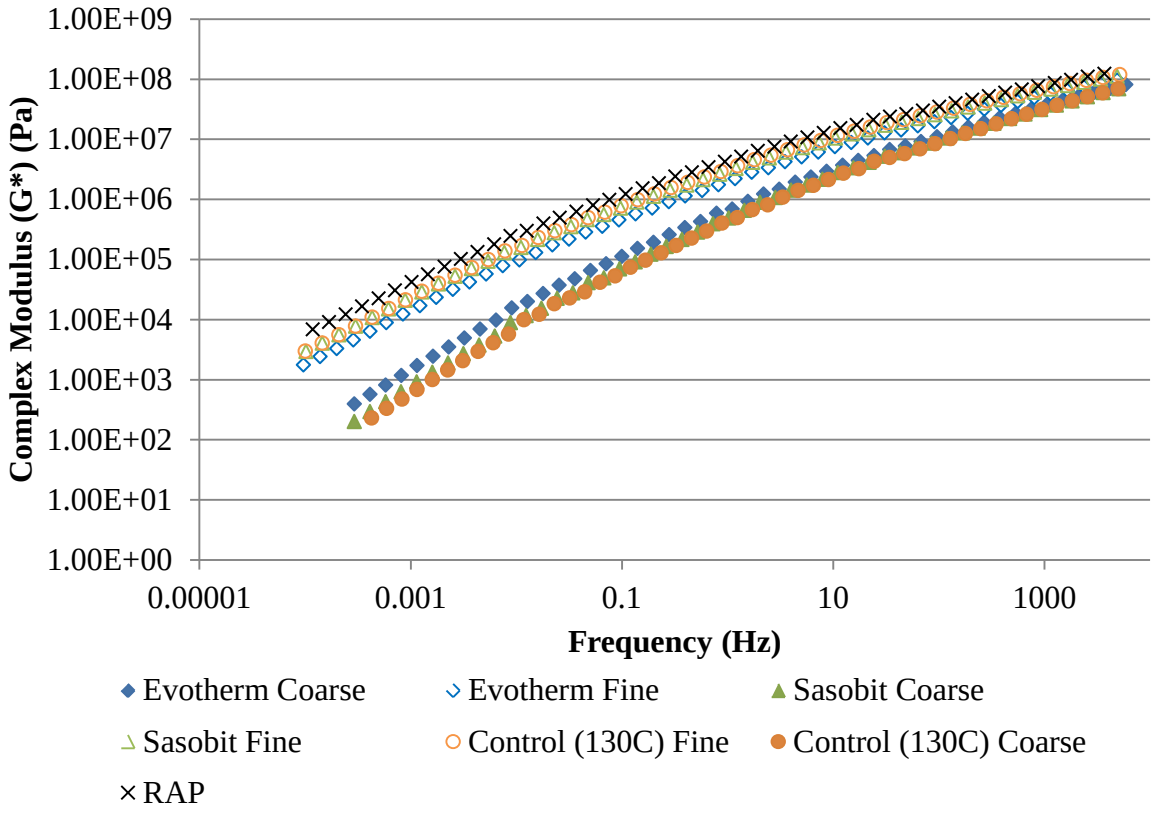


Figure 4.6 Master curve of the Complex Modulus (G*) for different WMA additives and a control mixture

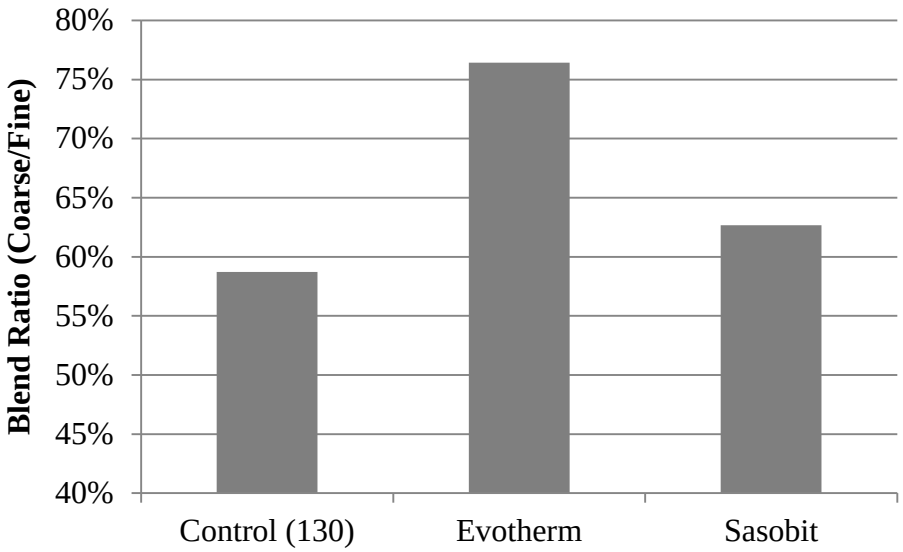


Figure 4.7 Blend Ratio for the 130°C control and WMA additives at 105 seconds of mixing

4.6 Conclusions

A study was conducted to evaluate the effects of mixing time, mixing temperature, and WMA additives on the blending efficiency of RAP and virgin binder. Studies were conducted using a large virgin aggregate, a PG64-22 virgin asphalt binder, and a "fine" aggregate RAP. After mixing, the aggregates were separated and the binders were recovered. The recovered binder rheology and molecular weight distributions were studied and yielded the following conclusions for the mix scenarios:

- Maximum blending ratio just below 80%
- As mixing time increases, so does the blending of the RAP binder with the virgin binder onto the coarse aggregate.
- Increasing the mixing time beyond 2.5 minutes (150 seconds) showed little to no influence, despite a relatively linear trend between blending time and blending efficiency.
- Mixing temperature played a significant role in the increase of the blending ratio from 59% at 130°C to 70% at 180°C.
- Mixing at a higher temperature of 180°C had no noticeable effect on the fine, RAP aggregate.
- When mixing with the WMA additive Evotherm at 130°C for 105 seconds a blend ratio of 76% was achieved, equivalent to that of the 160°C, 150 second control mixture. This shows that the Evotherm WMA additive has a positive effect on the blend ratio.

- The researchers found the Sasobit WMA additive to be the most workable of the mixtures at 130°C and seemed to achieve the best aggregate coating. It is suggested to investigate the effect of Sasobit at higher temperatures in future research.

CHAPTER V

REFINING LABORATORY PROCEDURE FOR ARTIFICIAL RAP: A COMPARATIVE STUDY

A version of this chapter was accepted for publication on November 2, 2013 by Benjamin F. Bowers, Baoshan Huang, and Xiang Shu:

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Benjamin F. Bowers was the principle researcher and author of “Refining Laboratory Procedure for Artificial RAP: A Comparative Study”. Benjamin’s contribution was conducting all literature review, testing, data analysis, and writing the text contained in the manuscript. Dr. Baoshan Huang and Dr. Xiang Shu provided guidance and ideas throughout the research process as well as editorial assistance.

5.1 Abstract

Laboratory aged, “Artificial RAP” is often used in controlled experiments in order to simulate the performance of paving mixtures containing RAP. Many different methods have been used to generate artificial RAP and they often modify the American Association of State Highway and Transportation Officials (AASHTO) R30 specification for oven aging gyratory compaction cylinders. Two modified AASHTO R30 methods were evaluated at 85°C and 115°C, as well as an artificial RAP created using PAV aged asphalt that had undergone one or two PAV cycles at 100°C and short term aging. A staged extraction procedure using trichloroethylene solvent was used to evaluate a four layered binder system around the aggregate. Each layer was studied with Fourier Transform Infrared Spectroscopy (FTIR) and an aging index is computed for comparison.

5.2 Introduction

The use of Reclaimed Asphalt Pavement (RAP) in pavement mixtures is of high priority to the asphalt paving industry due to its many sustainable and economic implications. Research is often conducted in a laboratory setting to evaluate the effectiveness of RAP within the pavement mixture. There are many factors that play into the performance of the RAP within the mixture that are being studied in controlled settings. Some fundamental research requires extremely sensitive testing techniques such as Fourier Transform Infrared Spectroscopy (FTIR), while others rely heavily on traditional macro-performance testing such as tensile strength ratio (TSR) or outputs of the Asphalt Mix Performance Tester (AMPT). Though the scope of applicable tests for RAP in new mixtures is large, there is often a need for a controlled RAP to evaluate the test results.

Much of the RAP milled from roads around the United States and worldwide is of an unknown origin. This may pose a problem in some controlled experimental designs because of the potential variability of the RAP binder when removed from the stockpile which may lead to differences in performance. Thus, in some cases it is necessary to create an “artificial RAP”, or a RAP with known properties, using traditional laboratory aging techniques. Many credible researches have relied on artificial RAP, sometimes alternatively named “laboratory produced RAP”, as a controlled variable within the study. However many of these studies rely on different methods of creating the artificial RAP. In general, a modification of AASHTO R30 “Standard Practice for Mixture Conditioning of Hot Mix Asphalt” is used where the long term aging process is

performed on a loose mixture rather than a compacted specimen is common. The objective of this research paper is to use a sensitive chemical testing technique, FTIR, to evaluate the current practice of artificial RAP creation along with a secondary methodology which relies primarily on the traditional binder aging techniques of the Rolling Thin Film Oven (RTFO) and the Pressure Aging Vessel (PAV) to ensure the best emulation of field RAP conditions. The objective of the research presented herein is to determine what practice of artificial RAP creation is best suited for controlled laboratory experiments. Four laboratory produced RAP methods are compared to two "true" RAP samples of known original PG grade using Fourier Transform Infrared spectroscopy.

5.2.1 Artificial RAP

In order to create an artificial RAP for a controlled study, Kvasnak et al. (2010) used the AASHTO R30 method while modifying the long term aging process by using a loose mixture that was stirred twice a day as compared to a gyratory compacted specimen called for in the specification. The intention of this study was to evaluate the RAP aggregate bulk specific gravity (G_{sb}) compared with the known G_{sb}. Kowalski et al. (2010) used the same method for developing artificial RAP with limestone, which is one of the worst aggregates in terms of pavement frictional resistance, in an investigation of how much RAP can be introduced into a new pavement mixture while not impacting the frictional properties. An artificial RAP had to be created for a study conducted by Huang et al. in 2005 which studied the impact of using RAP in Portland cement concrete (PCC)

(Huang et al. 2005b). The artificial RAP was created by aging an asphalt mixture with virgin PG64-22 asphalt binder for 12 hours at 120°C.

In 2011, Bennert and Martin (2011) published research on the use of polyphosphoric acid (PPA) modified asphalt RAP as more and more PPA modified roadways begin to reach their expected lifecycle. The researchers aged virgin mixtures containing PG64-22 asphalt binder for 2, 4, and 6 days at 100°C. The authors assumed that the binder makeup of a majority of the RAP in their focal area was originally a PG64-22, and they compared the artificial RAP binder to the extracted binder of the field-collected RAP. It was concluded that 8 days was actually required to reach the same binder characteristics of field-collected RAP. The final artificial RAP protocol consisted of short term aging the loose virgin mixture at compaction temperature for 2 hours, then long term age the loose mixture for 8 days at 100°C while stirring the mixture twice daily. This methodology was then applied to the creation of artificial RAP for Styrene-Butadiene-Styrene (SBS), PPA-SBS, and PPA modified asphalts for the study.

5.2.2 Chemical Testing Technique

One concern that is raised by the authors regarding the use of artificial RAP is whether or not the aging of the binder propagates completely through the binder film around the aggregate, or if the long term laboratory-aging process simply oxidizes and stiffens the outermost binder layer of the RAP particle. Though a method of investigating the aging

accuracy of an artificial RAP is to perform a traditional extraction and recovery of the asphalt binder to test it for comparison to field-collected RAP specimens, the assumption must be made that the binder has evenly aged throughout the film. The problem with this approach is that the inner most binder, that which is closest to the aggregate, may be significantly softer than that of the outer most binder which is further than the aggregate. This may influence the blending characteristics, and thus the performance, of a laboratory prepared specimen where the artificial RAP is mixed with virgin binder in efforts to study a RAP inclusive pavement blend.

To combat the concern of variability in the aging of the binder film in different artificial RAP cases, a staged extraction method can be applied. This methodology was proposed as early as 1979 by Zearley, as well as Carpenter and Wolosick, Huang et al., and Bowers et al. (Zearley et al. 1979, Carpenter and Wolosick 1980, Huang et al. 2005a, Bowers et al. 2014). The principle of this method is that solvent can be used to extract binder from a pavement mixture particle in layers by washing the mixture in specific time intervals. Each layer is collected in solution with trichloroethylene (TCE), a common asphalt solvent, and can be recovered and studied. By removing layers of the binder film, chemical testing techniques such as FTIR can be applied to evaluate the aging characteristics and determine how accurately artificial RAP compares the field-collected RAP. This method yields a higher confidence in RAP developed in a controlled setting.

It is important to know that aging or stiffening of asphalt binder occurs over time due to chemical changes, often conveyed through oxidation, within the medium. FTIR is a chemical testing technique which is used to determine the chemical functional groups within a given medium. These functional groups yield important information regarding the aging characteristics of the asphalt binder and some common functionalities which play an integral role in asphalt molecules are sulfoxides, anhydrides, carboxylic acid, and ketones, among others. A benefit of FTIR as compared to other testing techniques, as stated by Petersen (2009), is that unlike many other methods the asphalt binder can be tested as a complete system rather than having to fractionate the material for testing.

FTIR has been used in many researches specifically studying the effect of aging and oxidation on the chemical functionality of asphalt binder. Lu and Isacsson (2002) documented an increase in the carbonyl band (C=O) at approximately 1705cm^{-1}, which is contained in the ketone, carboxylic acid, and anhydride functionalities, as the binder ages. Production of ketones, as Petersen (2009) notes, is linearly related to an increase in the log viscosity. Lu and Isacsson found there was also an identifiable change in the sulfoxide band (S=O) at approximately 1030cm^{-1}. Changes in both of these bands are characteristic of oxidation of the binder. Huang and Grimes (2010) conducted similar tests but also compared the changes in the carbonyl band to results from the dynamic shear rheometer (DSR). The researchers were able to correlate the increase in the carbonyl band to the rheological shift factor of the DSR with a R^2 value of 0.95.

In a study of the aging characteristics of SBS copolymer modified asphalts, Negulescu et al. (2006) compared the carbonyl band around 1695cm^{-1} to that of the saturated C-C stretch at 1495cm^{-1} because the saturated C-C does not change much during the oxidation process. The researchers found that this ratio, henceforth referred to as the “aging index”, increases as the oxidation and aging increase. The same method of evaluating the FTIR spectra of asphalt was employed by Jia et al. (2014) when investigating the effects of waste engine oil residues in asphalt.

5.3 Materials and Methods

5.3.1 Materials

The artificial RAP was created using a 4.750 mm (#4) gravel and 9.51 mm (3/8 in) gravel. A PG64-22 binder was used to create the mix. Four mixtures were created, two oven aged and two PAV aged. The flow diagram provided in Figure 5.1 outlines the experimental program.

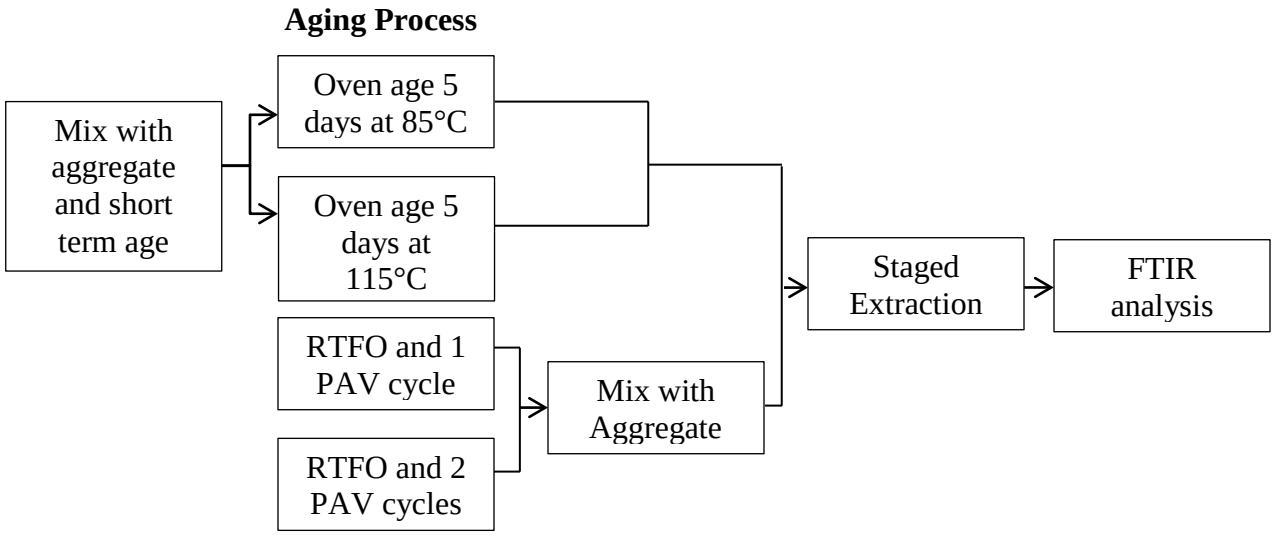

Figure 5.1 Diagram of experimental program

5.3.2 Oven aged mixtures

For the oven aged mixes, a pavement mixture was created containing 6% binder by mass. The binder was heated to 135°C and the aggregate to 160°C for two hours minimum. The binder was then added to the aggregate and mixed for 2 minutes or until the binder completely covered the aggregate in a tabletop mixer. The mixture was then placed into the oven spread out on a pan for 4 hours at 135°C in accordance to the short-term oven aging procedure prescribed in AASHTO R30-02. The mixture was then allowed to cool for 16 hours. The mixture was then spread onto two pans and placed into two draft ovens, one at 85°C and one at 115°C and allowed to age for 5 days.

5.3.3 PAV Aged Mixtures

Short term age conditioning was performed using AASHTO T240 with the RTFO. Binder was then separated and placed into the PAV for 16 hours at 100°C. Upon completion of one PAV cycle, binder was removed and prepared for mixing. This mixture can be referred to as 1xPAV. An additional PAV cycle of 16 hours at 100°C was then applied to some of the remaining binder. This binder mixture is referred to henceforth as 2xPAV.

In both cases, the 1xPAV cycle binder and 2xPAV cycle binder were put in separate vials and stirred while in a state of flow in order to ensure even distribution of aged binder. The mixture was then created by super heating the covered binder and aggregate to 180°C in a tabletop mixer for 2 minutes or until all aggregate was covered with binder.

5.3.4 Staged Extraction

Staged extraction was conducted using trichloroethylene (TCE), a common asphalt solvent. Approximately 20 grams of mixture was massed and placed into a basket. The basket was then washed in a beaker of solvent for 1 minute, then immediately removed and washed in the second beaker for a minute and so forth until 4 washes were complete. The mixture was allowed to sit in the fourth beaker until all visible asphalt binder was extracted from the aggregate. The solutions were then transferred to 20mL vials and labeled.

5.3.5 Rotoevaporation

Rotoevaporation was used to recover the asphalt binder from solution. The 20mL vial was rotated in water at 70°C under a vacuum until all solvent was evaporated. Once recovered, the vial with recovered asphalt binder was placed into a vacuum oven at 80°C overnight to remove any residual solvent that was not evaporated during the rotoevaporation phase.

5.3.6 Fourier Transform Infrared Spectroscopy

Figure 5.2 Binder sample after being drop cast for FTIR analysis

The recovered asphalt binder was drop-cast onto a 4mm potassium bromide (KBr) salt plate (Figure 5.2). Toluene was used to decrease the viscosity of the binder enough to cast the film. At the conclusion of the casting process the sample was placed into a vacuum oven at 80°C overnight to remove any toluene that was not evaporated by ambient temperature during the drop-casting process. The sample is then removed from

the oven and allowed to cool. A Nicolet FTIR was used for scanning at a ratio of 256 scans. Two replicates were made of each sample to ensure that the scans were accurate.

5.4 Results and Discussion

5.4.1 Extraction Differentiation

During the staged extraction process it was noted that the amount of material being removed in each "layer" of asphalt was significantly different. It was found for the AASHTO R30 prepared 85°C and 115°C samples that the shade of the solution was significantly lighter than that of the 1xPAV and 2xPAV aged samples. The AASHTO R30 prepared samples shown in Figure 5.3 are very dark through layers one and two, but begin to lighten significantly in layers three and four. The PAV aged artificial RAP shown in Figure 5.4 tends to have a noticeably darker complexion in layers three and four as compared to those created using the AASHTO R30 method. It is presumed that there is less asphalt to be removed in these layers and the asphalt that is being removed is likely a thin layer above the aggregate along with the absorbed asphalt within the aggregate.

Experience has shown that virgin, neat PG64-22 asphalt is very easily dissolved in TCE solvent. However, a PG64-22 RAP binder takes significantly longer to dissolve as indicated in Figure 5.5 where each of the four layers is equally dark in complexion. This would imply that the asphalt is less aged within the material and therefore less susceptible

to being dissolved by the solvent. This indicates that perhaps the traditionally accepted method of asphalt aging by using an open draft oven does not yield a uniformly aged binder through all layers.

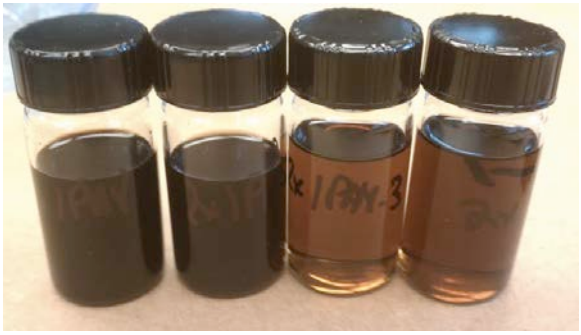

Figure 5.3 Example of PAV aged asphalt solutions. From left to right, layers 1-4.

Figure 5.4 Example of oven aged asphalt solutions. From left to right, layers 1-4.

Figure 5.5 PG64 RAP solutions. From left to right, layers 1-4.

5.4.2 Carbonyl Evaluation

After each binder was recovered the layers were tested using FTIR. The PG64 RAP and PG76 RAP were tested in triplicate and the artificial RAP mixtures were tested a minimum of four times per scenario. The aging index for each layer, defined by equation 5.1, was calculated based on the FTIR spectra (Negulescu et al. 2006, Jia et al. 2014).

$$Aging\ Index = \frac{Area\ of\ Carbonyl\ band\ at\ 1695\ cm^{-1}}{Area\ of\ saturated\ C{-}C\ band\ at\ 1455\ cm^{-1}} x100 \quad (5.1)$$

The following Figures 5.6-5.11 are indicative of the sample trends. The data shows the mean along with an error bar of 1 standard deviation from the mean for each sample layer.

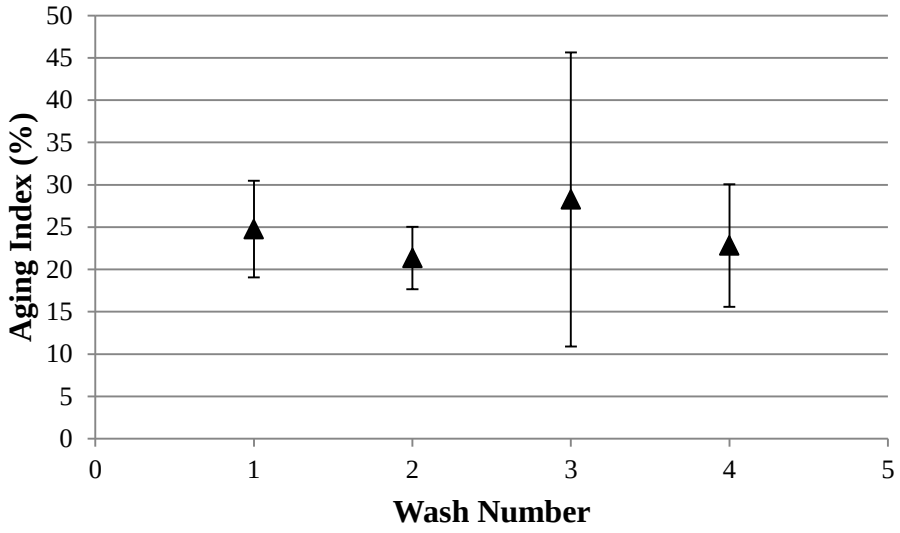

Figure 5.6 Aging index per layer for PG64 RAP

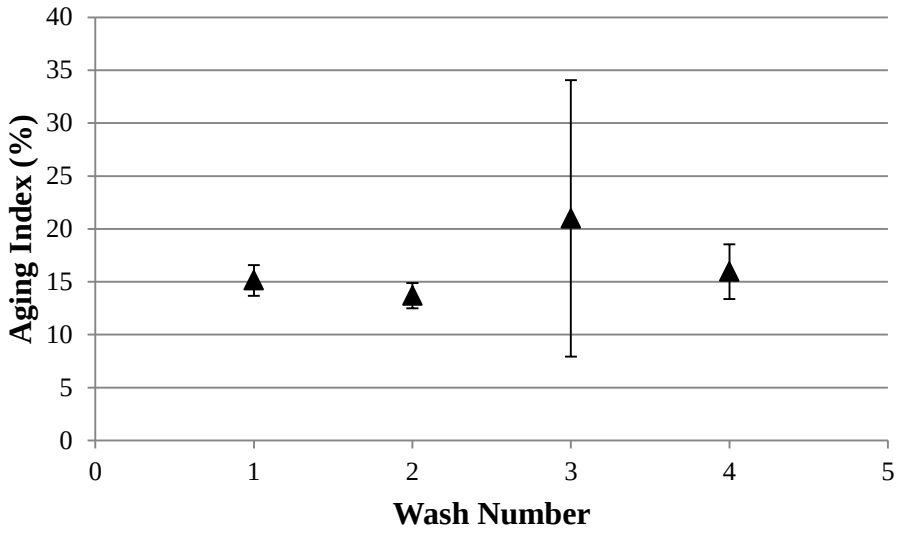

Figure 5.7 Aging index per layer for PG76 RAP

The analysis of the PG64 and PG76 RAP revealed variability in the layers. One might suspect a more systemic trend, such as increase in oxidation levels as you move from the outermost layer (1) to the inward most layer (4) due to the superheated aggregate severely oxidizing the binder during the mixing process. Another theory would be just the opposite, that because the long term aging occurs due to weathering and ambient conditions, the oxidation levels should decrease from the outside layer (4) in to the inner most layer (1) since the outmost layer is most likely to be exposed. The trend exhibited, however, is not a very consistent or indicative of either case. Both RAPs show that layer 3 has significant coefficient of variation (CV) 61.43% and 62.28% for the PG64 and PG76 RAP respectively. Furthermore, there is no established trend between the two RAP types. It is important to note that the aging index cannot be directly compared between these two RAP's because they have different binder sources and thus likely have different

areas for the saturated C-C stretch section of the FTIR spectra, which is used for normalization.

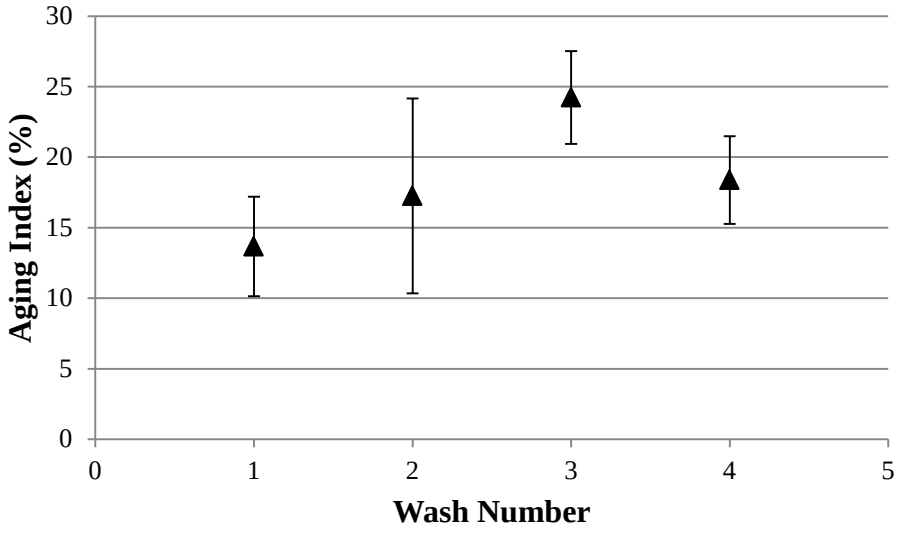

Figure 5.8 Aging index per layer for 85°C Artificial RAP

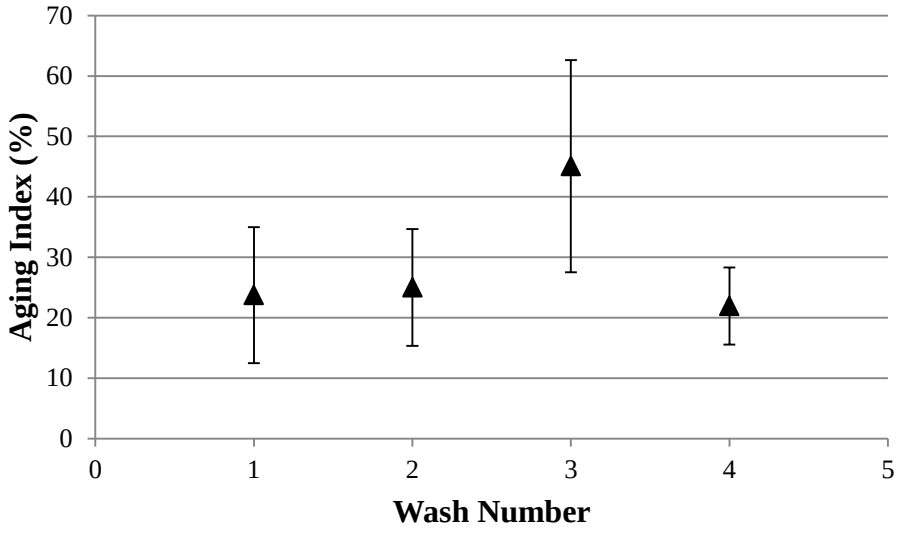

Figure 5.9 Aging index per layer for 115°C Artificial RAP

The artificial RAP binders which were aged using a modified AASHTO R30 methodology at 85°C and 115°C also exhibited variability similar to that of RAP. While it was apparent on the basis of aging index that the 85°C artificial RAP was significantly less oxidized than the 115°C RAP, the basic trend still remained the same. There is a peak of aging index at layer 3 when comparing the means of each layer. This hump, representing the most highly oxidized layer of the binder is layer 3 or the second innermost layer, is also indicative of the findings shown in Figure 5.4. There was very little binder which was extracted at this layer, indicating that perhaps most of the binder was already extracted in layers 1 and 2. This would mean that layer 3 is perhaps the innermost layer of binder and thus likely the most oxidized on the basis of its contact with the superheated aggregate during the mixing process. The maximum CV for the 85°C artificial RAP is 40.06% and an average CV of 24.10%. The maximum CV for the 115°C artificial RAP is 47.44% with an average CV of 38.53%. This further supports the idea that perhaps the modified AASHTO R30 yields an artificial RAP with higher variability, thus making it harder to predict the behavior of the RAP in a controlled laboratory experiment.

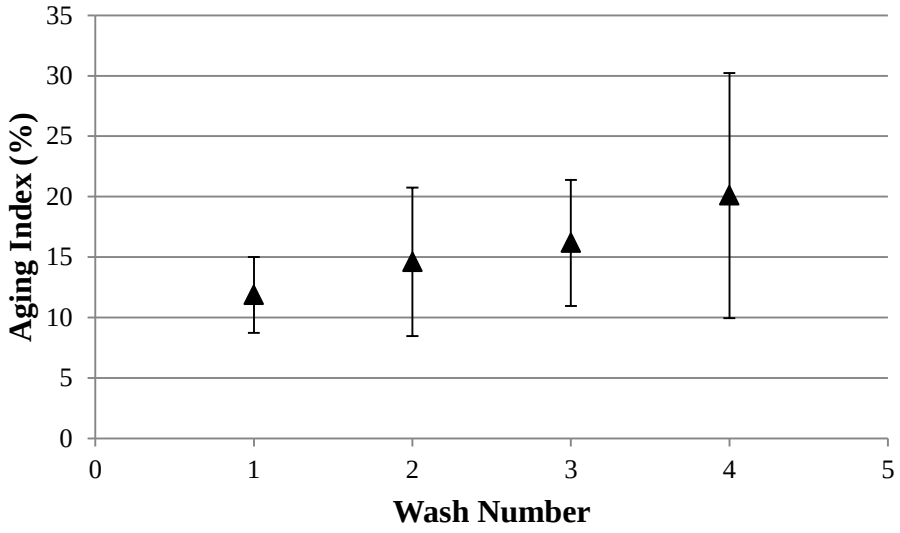

Figure 5.10 Aging index per layer for 1xPAV Artificial RAP

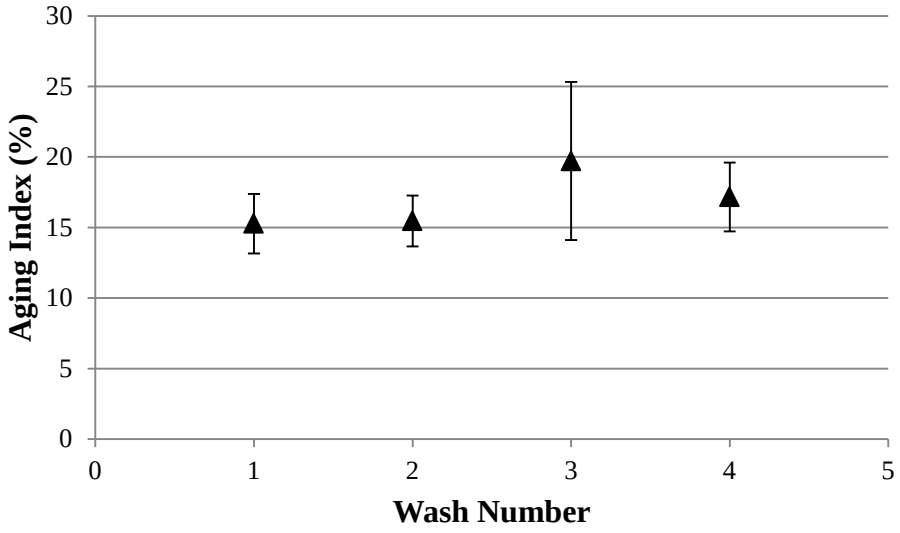

Figure 5.11 Aging index per layer for 2xPAV Artificial RAP

The RAP created using the Rolling Thin Film Oven and Pressure Aging Vessel provided comparable results. The variability was higher in the 1x PAV cycle samples with a CV of 37.79%; however an obvious trend was formed. This trend, with respect from the mean of each layer, shows an increase in oxidation from the outermost layer to the innermost

layer. This is likely due to the contact made with the superheated aggregate during mixing. Though oxidized through one PAV cycle already, the heat from the aggregate was still able to further oxidize the binder. This trend still maintained variability, likely because the amount of carbonyl growth due to the superheated aggregate can vary depending on how and when the binder came into contact with the aggregate.

Two PAV cycled artificial RAP (2xPAV) proved to have the least variability in the data set with a CV of 17.01%. The mean values of the aging index for each layer remained between 15 and 20%, closer than any other sample set. There is also no upward trend in aging index from the outermost layer to the innermost layer, showing the influence of the superheated aggregate during mixing, unlike the 1xPAV data set. This is believed to be because of the increased oxidation experienced by the 2xPAV artificial RAP when it underwent the second PAV cycle at 100°C.

A one-way analysis of variance (ANOVA) was conducted to evaluate the layers of each of the four artificial RAP types. The null hypothesis is that the means for each layer of a given artificial RAP sample are equal. If the null hypothesis is found to be true the artificial RAP is considered ideal for a controlled laboratory experiment because it is predictable. The one-way ANOVA test was conducted with an $\alpha = 0.05$. Both the PAV aged RAPs were found to have no significant differences in mean values for all layers with a p-value of 0.22 for the 1xPAV artificial RAP and a p-value of 0.17 for the 2xPAV artificial RAP. The artificial RAP that was oven aged at 115°C had a p-value of 0.07,

which is barely acceptable while the 85°C oven aged artificial RAP had a p-value of 0.01 which rejects the null hypothesis that the means between layers are equal.

Though the p-value for the 1xPAV artificial RAP was slightly higher than that of the 2xPAV artificial RAP, the 2xPAV RAP still provided a higher average mean with respect to aging index. This indicates that the 2xPAV artificial RAP binder has experienced more aging which may make it more suitable to be used as an artificial RAP. While it is of little surprise that the field collected RAP exhibited variability, it was of relative surprise that the modified AASHTO R30 oven aged RAP exhibited such increased variability within the same layer. This indicates however that perhaps the modified AASHTO R30 RAP does present an artificial RAP that is more representative of the field collected RAP. The problem with this methodology could prove to be the lack of experimental control. There are certainly cases where a more variable artificial RAP sample may be desirable, but for most controlled experiments it is recommended to use an artificial RAP using the 2xPAV design method.

5.5 Conclusions

Four artificial RAP methodologies were used in this experiment and compared. Additionally, two field collected RAPs with known origin (PG64-22 and PG76-22) were tested for comparison as a control. The staged extraction method was employed to test

the layered binder system and the variability of oxidation within the layers using FTIR. The results were statistically analyzed and the following conclusions were drawn:

- There is variability in the oxidation levels of the field collected RAP even within the same layer. This shows that RAP is not uniform in oxidation trend, but rather highly variable.
- There is variability in artificial RAP prepared using a modified AASHTO R30 method at 85°C and 115°C. The trend in mean values is similar to that of the field collected RAP
- The 1xPAV artificial RAP exhibited a clear increase in oxidation levels from the outermost layer to the inner most layer, likely due to the superheated aggregate during mixing.
- The 2xPAV artificial RAP showed the least variability in layers with a CV of 17.01%, as well as with respect to mean oxidation levels. There also is no effect of superheated aggregate on the binder.
- A one-way ANOVA analysis of the four layer system revealed that the mean values for the 85°C artificial RAP were not equal while the 1xPAV, 2xPAV, and 115°C did not exhibit a statistical difference in mean values.
- The staged extraction method revealed that field collected RAP and the PAV aged RAP yielded an increased amount of soluble binder later in the staged extraction process (i.e. layers 3 and 4) while the modified AASHTO R30 samples did not seem to have any binder remaining to be dissolved later in the process.

- The 2xPAV artificial RAP method is advised for laboratory experiments which require an artificial RAP.

CHAPTER VI

NEW METHOD FOR DETECTING ASPHALT CONTAMINATION WITHIN A FINE AGGREGATE MEDIUM THROUGH CHEMICAL TESTING

A version of this chapter was originally published by Benjamin F. Bowers, Baoshan Huang, and Xiang Shu:

Bowers, B.F., Huang, B., and Shu, X. (2013). "New Method for Detecting Asphalt Contamination within Fine Aggregate Medium through Chemical Testing". *Journal of Materials in Civil Engineering.* V25(2), p.252-256. May 2013.

Benjamin F. Bowers was the principle researcher and author of "New Method for Detecting Asphalt Contamination within Fine Aggregate Medium through Chemical Testing". Benjamin's contribution was conducting all literature review, testing, data analysis, and writing the text contained in the manuscript. Dr. Baoshan Huang and Dr. Xiang Shu provided guidance and ideas throughout the research process as well as editorial assistance.

6.1 Abstract

A method has been developed using gel permeation chromatography (GPC), also known as size exclusion chromatography (SEC), for examining extracted material from fine aggregate to identify asphalt contamination within the fine aggregate. The development of this method was initiated after the research group was contacted by a major contractor who voiced concern over potential asphalt contamination of fine aggregates. The problem with fine aggregate contamination lies in the altering of optimum asphalt content and the resulting change in asphalt performance grade. Contamination is brought about due to the presence of small amounts of asphalt cement that are not detectable by the naked eye. This study evaluated two sands of known origin which were contaminated with PG64-22 asphalt and one sand contaminated with PG82-22 asphalt, all at very low percentages. A traditional method of asphalt content testing, the AASHTO T308 ignition oven method, was compared to the newly developed method. For the GPC sampling, soxhlet extraction was performed on fine aggregates using the asphalt solvent tetrahydrofuran (THF). The

recovered material was then injected in solution into the GPC for evaluation. It was concluded that the GPC method yields convincing evidence of asphalt contamination as well as a more accurate estimation of percent asphalt contamination within fine aggregate.

6.2 Introduction

Fine aggregate is used in asphalt mixtures to obtain the desired density and strength as well as modifying the asphalts rheological properties. Fine aggregates are typically defined as aggregates passing 2.36 mm (#8) or a 2.00 mm (#10) sieve and are used to increase the aggregate surface area within the mixture, which in turn affects asphalt content (Asphalt Institute 2001, AASHTO 1965, Chapuis and Legare 1992). Fine aggregates come from many different sources and could be contaminated with other materials (such as asphalt) without being noticed. In asphalt pavement construction, it is critical to achieve the optimum asphalt content selected in the mixture design in order to ensure the anticipated performance of asphalt pavement. If asphalt is unaccounted for within the contaminated fine aggregate, there could be error in the actual asphalt content as well as the performance grade of the final asphalt pavement mixture, which could result in premature failure within pavement structure.

There are currently several methods of determining the asphalt content within an asphalt mixture. Two frequently used methods are AASHTO T308 “Determining the Asphalt

Binder Content of Hot-Mix Asphalt (HMA) by the Ignition Method", which uses an ignition oven, and AASHTO T164 "Quantitative Extraction of Asphalt Binder from Hot-Mix Asphalt (HMA)", which uses chemical extraction techniques to determine the asphalt content. Though these methods may be used to detect the presence of asphalt within fine aggregate, they are primarily used to determine the asphalt content of an HMA mixture as opposed to fine aggregate contaminated with a very low content of asphalt.

The basic principle of the ignition method (AASHTO T308) is measuring the weight loss that occurs in a 1200g (minimum) sample at 578°C (1072°F) due to asphalt burn-off. A problem associated with this methodology is that there is an excessive loss on ignition during the test, caused by aggregate breakdown. Therefore, AASHTO T308 requires that at least two to four specimens be tested with a known asphalt content to determine the mineral matter loss due to ignition. In addition to ordinary ignition oven method, there is also an infrared furnace (oven) method, which produces a different correction factor. Hurley and Prowell (2003) investigated the difference in correction factor but found that it had little or no effect on the final asphalt content.

The quantitative extraction method (AASHTO T164) involves extracting asphalt from HMA mixture by means of chemical solvents. The solvents include ammonium carbonate, methylene chloride, normal-propyl bromide, trichloroethylene, and/or terpene. Like the ignition oven method, mineral matter needs to be accounted for when calculating

the percentage asphalt content. This is done by one of the following methods as listed in AASHTO T164 section 11.6: ashing method, centrifuge method, or volumetric method. Sample sizes for AASHTO T164 range from 0.5-4 kg.

Methods outlined in AASHTO T308 and T164 are applicable to calculating the percentage of asphalt present within an HMA mixture. These methods are not, however, best suited for the detection of asphalt contamination within fine aggregate, which may not be visible to the naked eye. Without knowing that asphalt is indeed present, it would be difficult to tell the difference between asphalt contaminant and "mineral matter" present in the ignition loss and/or extraction of the fines. A method needs to be developed to address the presence of asphalt contamination within fine aggregate. Two possible methods for determining contamination within a fine aggregate are Gel Permeation Chromatography (GPC), which was studied in the scope of this Chapter, as well as Fourier Transform Infrared Spectroscopy (FTIR). Both methods may be used to characterize a medium by way of chemical analysis.

Gel Permeation Chromatography (GPC), also known as size exclusion chromatography (SEC), is a chemical testing technique that is often applied to polymer testing, but has also been used in the testing of asphalts. McCann, Rovani, and Thomas (2007) used GPC to successfully detect polymers such as styrene-butadiene-styrene co-polymer within asphalt binders. Lu and Isacsson (2002), Siddiqui and Ali (1999), Kim and Burati (1993), Churchill et al. (1995), and S.J. Lee et al. (2009) used this technique to study the effects

of asphalt aging. GPC was used by Snyder (1969) to determine asphalt molecular weight distributions. Gilmore et al. (1983) determined the presence of antistripping agents within asphalt cement by use of GPC. Kim et al. (2006) estimated recycled asphalt pavement (RAP) binder viscosity while comparing both traditional binder recovery and a new solvent only-method (tetrahydrofuran) for binder recovery for GPC application. The effect of crumb rubber modification of binders has been studied using GPC by Shen et al. (2010), Lee et al. (2010), and Daly and Negulescu (1997). Past researches have indicated that GPC can be easily applied to the study of asphalt. However, its potential use as an indicator of asphalt presence has not previously been investigated.

The aim of GPC is to separate different molecules by their individual molecular sizes. The GPC column is packed with beads of varying porosity. This causes the variant molecules to pass through the column at different rates. As the molecules exit the column, the refractive index (RI) or UV absorption can be detected. The higher each of these values appears over the elution time, the higher the presence of molecules of a specific molecular size. Larger molecules elute faster because their large size excludes them from passing through the packing pores in the column. Smaller molecules will pass through these pores, causing them to elute at a slower rate (Malvern 2011). This study outlines a method of using GPC for determination of asphalt presence in very small quantities within a medium.

6.3 Objectives and Scope

The objective of this research is to develop a more sensitive method of detecting asphalt contamination within a fine aggregate medium using GPC. Two fine aggregates were tested, a mechanical (crushed) sand and a river sand, and each was contaminated with PG64-22 asphalt. Additionally, the river sand was also contaminated with a second asphalt of a different performance grade, PG82-22. The ignition oven test was conducted and compared with a new method which utilized soxhlet extraction followed by testing the recovered material using GPC.

6.4 Experimental Program

6.4.1 Contamination

Two fine aggregates were collected from a laboratory stock pile for testing: mechanically separated sand and river sand (delineated as MS and RS respectively). Both fine aggregates passed a #10 sieve and were placed in an oven at 105°C (221°F) to remove moisture within the aggregate. The fine aggregates were massed into their appropriate specimen amounts of 1200 grams for the ignition oven testing and 50 grams for the GPC testing. The fine aggregate was then contaminated with asphalt (PG64-22 or PG82-22) in small percentages by weight (<1.4%). The asphalt contaminant was not further mixed within the aggregates due to the potential that there would be a loss of asphalt to the mixing bowl and apparatus. Given the types of testing performed it is important to know

the exact amount of asphalt contaminant that is present in the mixture. Furthermore, due to the extraction and burnoff characteristics of the two methodologies, uniform mixing assumed not be necessary to achieve the correct result. In the case of extraction, the entire mixture is repeatedly soaked in the solvent, thus removing all soluble portions of the mixture including the asphalt.

6.4.2 Ignition Oven Method

An NCAT Ignition oven was used for the ignition oven testing. The procedures outlined in AASHTO T308 were followed. Samples were massed in the ignition basket both prior to and after testing. Once complete, the percentage loss on ignition was calculated and compared to percentage of contaminant present. A calibration factor was then calculated based on AASHTO T308.

6.4.3 Extraction Method

Extraction of asphalt from contaminated samples was performed using a Soxhlet extractor. The contaminated fine aggregate was placed carefully in the extraction thimble and then placed into the extractor. Tetrahydrofuran (THF) with 100ppm butylated hydroxytoluene stabilizer was used as the extraction solvent. Once the apparatus was assembled, the extractor was filled with THF. Extraction continued overnight until the solvent became clear and colorless.

Once extraction was complete, the solvent was evaporated from the extracted material using a rotoevaporator. When small amounts of solvent remained in the flask, a syringe was used to remove the solution from the flask and place it into a vial. Before injecting the solution into the vial it was passed through a 0.45μm filter. The flask was then rinsed with THF to remove any remaining extracted material, which was then transferred to the vial. The vial was then rotoevaporated to remove the remaining THF. Once complete, the vial was placed into an oven with a vacuum overnight at 80°C (176°F) to remove any remaining solvent. Finally, the weight of the extracted material was measured and recorded.

It is important to note that THF was used as the extraction solvent primarily for two reasons: 1.) It is a strong asphalt solvent as referenced by Kim et al. (2006), and more importantly 2.) the GPC used for experimentation used THF as its mobile phase. Other solvents, such as those listed in AASHTO T164, could be used for extraction and then rotoevaporated.

6.4.4 Gel Permeation Chromatography

Gel Permeation Chromatography was performed using a TOSOH EcoSEC GPC model HLC-8320GPC. It contained two columns in series packed with multi-pore polystyrene divinylbenzene copolymer. THF was used as the injection solvent at 100uL. The extracted material was in a 1mg/mL solution and passed through a 0.2μm filter. Each

sample was tested over a 15 minute elution period at 40°C. The EcoSEC analysis software was used for initial data comparisons but the data was exported into Microsoft Excel for final comparisons.

6.5 Results and Discussion

6.5.1 Ignition Oven Method Results

The results from three ignition oven tests, as summarized in Table 6.1, show a difference beyond the AC contaminant of approximately 0.71% in the case of the river sand (RS) and 1.195% in the case of the mechanical sand (MS). MS-1 was not considered in this due to the vast difference in result.

Table 6.1 Ignition oven results (%Mass)

Sample	Added AC (%)	Percent burnoff (%)	% Burnoff - % Added AC
RS-1	0.27%	1.04%	0.77%
RS-2	0.26%	0.97%	0.71%
RS-3	0.25%	0.96%	0.71%
MS-1	0.25%	0.91%	0.67%
MS-2	0.25%	1.45%	1.20%
MS-3	0.27%	1.45%	1.19%

It is important to note that the AC percentage is known in all of these tests. In the case of fine aggregate contaminant testing, there is approximately 0.91 to 1.45% by weight of material that was lost in ignition. Because it is difficult to determine what percentage of

this material was asphalt as compared to aggregate degradation or mineral matter loss, it is nearly impossible to give an accurate estimation of asphalt content.

One method for combating this issue while maintaining use of the ignition oven would be to test and calculate a loss on ignition on clean/non-contaminated aggregate from the same source. Still, the data presented in Table 6.1 indicate that there is variability in results between the same aggregate, often less than one percent. The fine aggregate asphalt contamination may only be a fraction of a percent. Therefore due to the variability of the test results, it is difficult to tell whether the percentage differences are because of asphalt contamination or simply variability in aggregate ignition.

6.5.2 Extraction Method Results

The percent difference between the extracted material and the known asphalt content of each sample (Table 6.2) is less than 0.1% in the river sand (RS), with the exception of RS-4. In the mechanical sand (MS) the results are more variable. These differences are attributed to the mineral matter within the aggregates which are soluble in THF. This differentiation is further resolved by examining the GPC outputs provided in Figures 6.1, 6.2, and 6.3, to be further explained in the following sections. The Extracted RS and Extracted MS, as noted on the figures, are solutions made of material that was soluble in THF and therefore adept to being extracted. Without the presence of this soluble material in the aggregate there would be no ability for the GPC to detect molecular weight

changes. Thus, the positive variation as represented in Table 6.2 is to be expected. The loss of weight as displayed in RS-4 and MS-5 may be explained by the transfer of material from extraction flask to the rotoevaporation vial, which included filtration through a 0.45µm filter.

Table 6.2 Extraction method results

Sample	% A/C	% Extracted	% Difference
RS-4	0.36%	0.20%	-0.16%
RS-5	0.42%	0.46%	0.04%
RS-6	0.52%	0.57%	0.05%
MS-4	0.60%	0.60%	0.00%
MS-5	1.36%	1.17%	-0.19%
MS-6	0.62%	0.93%	0.31%

In comparison to the ignition oven method, simply extracting material from the fine aggregate with THF is much more precise. However, it is important to note that this method alone does not validate that the fine aggregate is contaminated with asphalt. Conclusions on the variability are drawn simply because all testing was performed with a known asphalt contamination.

6.5.3 Preliminary GPC Analysis

Preliminary tests were performed using a sand of unknown origin to validate whether GPC could be used to indicate whether a fine aggregate is contaminated with asphalt. The sand was contaminated with PG64-22 asphalt at approximately 0.2% by weight, a level low enough that when dispersed throughout the aggregate it would be assumed to not be

detectable by the naked eye. After extraction, the solution created from the contaminated sand was injected at 1 milligram of recovered material per one milliliter of elution solvent (THF) and compared to extracted virgin sand and virgin PG64-22 asphalt injected at the same concentration. This data is shown in Figure 6.1. It is clear that the contaminated sand contains asphalt when compared to both virgin asphalt and the virgin sand for two reasons: 1) The asphalt appears at a much higher concentration earlier in the elution curve (~9 – 11.5 minutes) than the sand (~10.5 – 11.5 minutes), and 2) the organic material (mineral matter) appears in the contaminated sample as a second peak, which should occur in accordance with the virgin sand curve. These peaks, the first of which is related to the virgin asphalt, relate to the approximate molecular weight at which the most molecules in the sample are present.

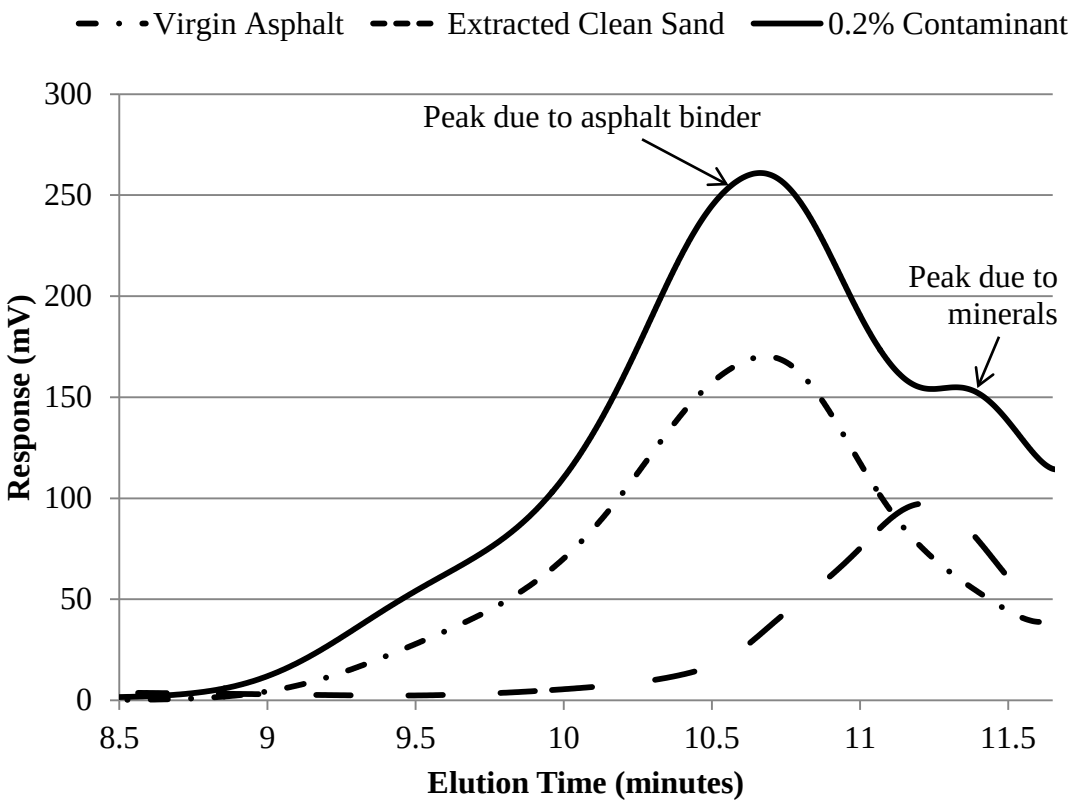

Figure 6.1 GPC chromatograms from preliminary validation of tests

6.5.4 GPC Analysis of River Sand and Mechanical Sand

It is clear when examining the GPC output for both the RS and MS at a 1 mg/mL concentration which specimens are contaminated and which is not. Asphalt contains more molecules of high-molecular weight causing it to appear much earlier in the elution period and at a much higher rate. This is also shown by the virgin PG64-22 and PG82-22 curves in Figure 6.2 and Figure 6.3. The data reveal that the MS contains more extractable material (mineral matter) than the RS, but the molecular weight distribution is very similar. It is clear that there are differences between each of the specimens through

their output variability. The GPC analysis proved to be repeatable over each of the different extractions as well as by comparing Figure 6.2 and Figure 6.3 in that the molecular weight distribution of the contaminated sand closely resembles that of the asphalt binder as compared to the mineral matter extracted from the sand.

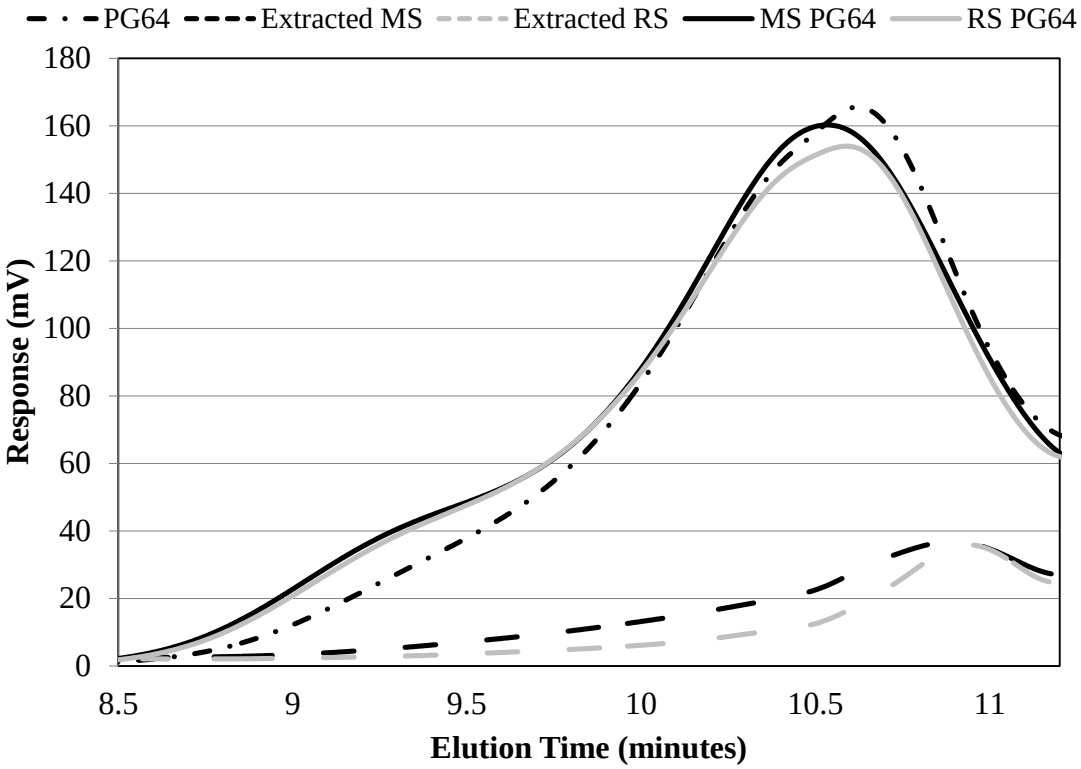

Figure 6.2 GPC chromatograms of contaminated and non-contaminated river sand and mechanical sand with PG64-22 asphalt

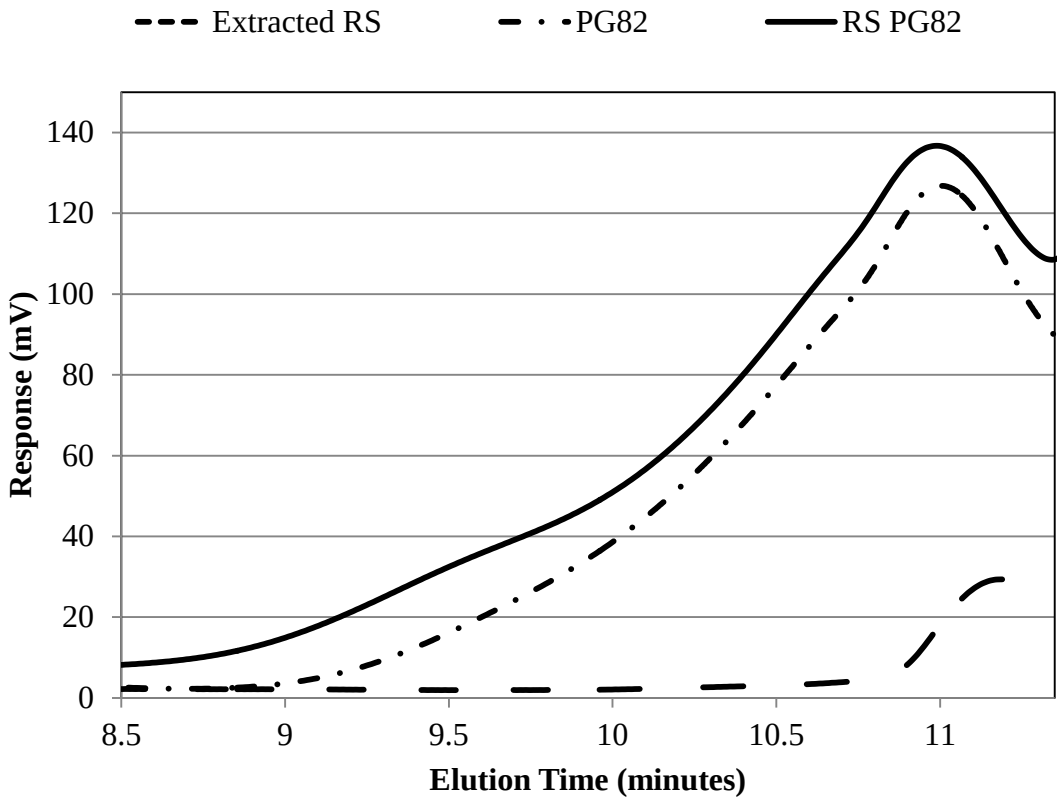

Figure 6.3 GPC chromatograms of contaminated and non-contaminated river sand with PG82-22 asphalt

It is important to note that a second peak, which would clearly indicate the presence of mineral matter in the sample, does not appear in the chromatograph of the contaminated specimens. The absence of this peak can be explained by the size distribution and lower concentration of molecules of similar size within the sand. In this case, distribution levels and the larger size of the molecules are limited. This causes the disappearance of the second peak even though the molecules provided by the mineral matter are present. However, it is also conclusive which specimens are contaminated and which are not when comparing the contaminated chromatographs to the virgin MS and RS chromatographs, indicating repeatability between specimens of both the same and

different types. In the case of the contaminated aggregates with either grade of asphalt, there was a drastic increase in high molecular weight material as compared to those of the aggregates without contamination. The asphalt chromatographs also compare closely to each other and to the data in the literature. Based on this study, contamination is clearly indicated by the presence of higher molecular weight material, which is comparable between different grades of asphalt. Therefore, one could assume that to determine whether an aggregate is contaminated with asphalt a comparison of the suspect aggregate extract to various grades of asphalt would resolve a reasonable conclusion. In this case, if a clean aggregate cannot be found for comparisons to be made in the percentage of extractable material, it would be difficult to calculate exactly how much asphalt is present. Nonetheless, according to the data herein an estimation of percent contamination could be made with an upper bound of roughly 0.3% while most samples were within 0.1% by weight, as demonstrated in the percent difference presented Table 6.2. Meanwhile, ignition oven results yielded at least a full degree of magnitude higher (0.7 to 1.2%) as shown in Table 6.1 in comparison to the same source materials studied with the extraction method.

6.6 Conclusions

It is important to know if fine aggregates used in an asphalt mix design are contaminated with asphalt to prevent pavement performance failure. Extraction of fine aggregates with tetrahydrofuran (THF) along with the application of Gel Permeation Chromatography

(GPC) can be used as a repeatable alternative method for detecting small amounts of asphalt contamination contained within a fine aggregate medium. When the percent of extracted material is compared to the loss of ignition from the ignition oven, the extraction method with THF proves to be much more accurate. The following methods may be used to determine whether the fine aggregate is contaminated:

- If uncontaminated fine aggregate of the same type and source is available, it can be used to compare the percent of extracted material as well as the GPC output to the suspect fine aggregate. Aggregates contaminated with asphalt will likely have the presence of significantly higher molecular weight material as compared to that of non-contaminated aggregate.
- Asphalt can be injected at the same concentration as the extracted material from the fine aggregate into the GPC in order to compare the intensity of the output along with the appearance of the material in the elution time. It is recommended if this approach is taken alone that a suite of asphalt samples of varying type and source are used for comparison. Worth noting is that the PG64-22 and PG82-22 asphalts used in this study had extremely similar chromatograph outputs. This finding is consistent with past asphalt related GPC literature.
- When examining the GPC output of the suspect fine aggregate, a second peak in the chromatograph may indicate the presence of mineral matter.

6.7 Article Acknowledgements

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CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

A series of studies were conducted that applied analytical chemistry techniques to shed light on and solve problems that have been plaguing the asphalt paving industry. Gel Permeation Chromatography (GPC) and Fourier Transform Infrared Spectroscopy (FTIR) were used to investigate these problems on a molecular scale in conjunction with traditional asphalt performance tests. At the completion of these studies, the following conclusions have been reached:

1. The sequential dissolution of asphalt binder in common asphalt solvents such as trichloroethylene, tetrahydrofuran, and toluene, as well as a more uncommon asphalt solvent, decahydronaphthalene, has been found to occur in some cases. Trichloroethylene did not appear to have any significant sequential dissolution characteristics. Toluene, when compared to decalin, may sequentially dissolve the maltene fraction prior to dissolving the asphaltene fraction of the bitumen. However, this case shed light on the benefit of faster dissolution kinetics (toluene) as compared to slower dissolution kinetics (decalin) in that the faster solvent tends to have less variability and minimal sequential dissolution. Tetrahydrofuran was found to behave sequentially in accordance to fractionation studies. This is in agreement with the calculations based on the Hansen Solubility Parameters provided in the work of Redelius (2004) and Hansen (2000).
2. Characterization of a virgin mixture with gel permeation chromatography (GPC) found little to no difference in the large molecular sizes (LMS%) for different

layers of binder, further confirming that the staged extraction methodology is viable using trichloroethylene. Mixtures characterized with GPC and FTIR had similar findings that support partial blending occurs between all layers of the tested mixtures. FTIR was found to be a more sensitive test method, but certain variables such as RAP source should be considered due to the limitations presented in data normalization (e.g. differences in the saturated C-C stretch band).

3. When evaluating different mixing scenarios that include RAP, comparisons between the dynamic shear rheometer complex modulus master curve and the blending ratio calculations based on LMS% between recovered binders were found to be in agreement. However, the blending ratio was able to provide a numerical comparison that shed light on how much blending between RAP and virgin binder actually occurs. Mixing conditions and the inclusion of warm mix asphalt additives were found to affect the efficiency of the blend. A threshold mixing time was found to be at 2.5 minutes. Increased mixing temperatures to 180°C did not appear to have a negative impact on the RAP by means of oxidation, and there was a noticeable increase in blending efficiency. Warm mix additives were found to have a beneficial impact on the increase in blending ratio. Evotherm was found to have a blending efficiency at 130°C for 1.75 minutes nearly equivalent to that of a 160°C, 2.5 minute mixture. All mixtures had less than 80% blending ratio.

4. Four different methods were applied to creating an optimum artificial RAP for controlled laboratory experiments. The results of the carbonyl index as defined by the FTIR and a one-way ANOVA analysis of results found that the 2xPAV aged mixture was the best in terms of a controlled artificial RAP. However, it was also found that both of the true RAP samples had increased variability between layers, making the 2xPAV aged RAP not a true simulation of a field collected RAP.
5. Traditional testing methods were found to not have the sensitivity, and thus the ability to detect the contamination of fine aggregates with asphalt that is not detectable to the naked eye. Gel permeation chromatography, in conjunction with soxhlet extraction, was found to be a robust method of detecting this contamination.

7.2 Recommendations

The work presented in this study investigates the blending efficiency problem using chemical testing techniques that can be related to performance properties commonly considered in asphalt paving. Furthermore, the study investigates the application of some of these techniques to successfully solving some specialized problems within the asphalt paving industry. On the basis of the research presented herein, some considerations for future work are recommended as follows:

1. This study presents encouraging data with regard to the use of staged extraction to evaluate the blending efficiency of RAP in pavements. It is recommended that

further research be conducted looking at both virgin and RAP aggregates, as well as by changing mixing parameters similar to those outlined within the scope of this study to investigate how binder diffusion changes. It is suspected that at a tipping point, a 100% blend will be achieved and the LMS% will be equal amongst all layers.

2. The use of warm mix additives was found to enhance the blending efficiency of RAP in mixtures. It is recommended that further study be conducted looking at different warm mix additives, including but not limited to foaming, as well as changing the mixing parameters for the WMA additives studied herein.
3. The sequential dissolution of other solvents that are gaining interest in the asphalt community such as *n*-propyl bromide should be investigated as a possible alternative to trichloroethylene.

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APPENDICES

A.1.0 Procedure for Gel Permeation Chromatography and Data Analysis

A.1.1 Important Notes of Consideration

Make sure that the lab/equipment manager has given the proper training to operate the GPC equipment prior to testing. Also talk to the lab manager about how to keep track of the materials you use in the lab so that they can all be reported and properly charged to a research account.

Materials will include:

- Scintillation vials
- Auto-sampling vials and caps specific to the GPC
- Auto-sampling cap crimp
- Tetrahydrofuran solvent
- 0.2 micron filters
- Transfer syringe

Asphalt in solution is injected into the GPC column at a concentration of 1 milligram of asphalt cement per 1 milliliter of solvent. The solvent for the EcoSEC GPC is tetrahydrofuran (THF), which asphalt is soluble in.

Important: Be sure to read the Material Safety Data Sheet (MSDS) for tetrahydrofuran so that there is a clear understanding of the risk of working with THF. Ensure that you have the proper protective equipment when working with THF (gloves, lab coat, glasses, etc.). The MSDS can be found at the Fisher Scientific website, along with a number of other websites.

A.1.2 Sampling

- Using a microbalance, mass the asphalt binder sample and place into a 20 mL scintillation vial
    - **Tip:** Keep this below 20 mg of asphalt binder
- After massing the asphalt binder, take the recorded amount in milligrams and multiply it by the density of your elution solvent, tetrahydrofuran (THF) to calculate how many grams of THF are required to reach 1 milligram of asphalt cement per milliliter of THF in solution, also written 1 mg/mL. The density of THF is 0.8892 g/mL
    - **Example:**

      10 mg of asphalt binder

      1 mg/mL concentration of solution

      10 mg / 10 mL = 1 mg/mL so 10 mL of THF solvent is needed

      10 mL x 0.8892 g/mL = **8.892 grams of solvent to be added to asphalt binder**

- Add the THF solvent to the scintillation vial, carefully watching the mass change on the microbalance.
- Once the solvent has been added, close the cap of the vial. Ensure that an *aluminum foil lined cap* (or a cap that is not lined with cardboard material) is used.
- Shake the solvent using a shaker or a spinning apparatus for a minimum of a minute at high speed, or up to 5 minutes at low speed. Hold the sample up to light to ensure that the asphalt binder has completely dissolved in the solvent.
- **Tip:** Do NOT allow samples to sit overnight in solution. Experience says that this will begin to change your output.
- **Tip:** It is advised to run as many samples at once as possible to limit any external factors from altering your data

A.1.3 Preparation of auto-sampler vials/samples

- Collect and properly label the auto-sample vials that are designed for the EcoSEC GPC
- Clean the transfer syringe using THF to ensure that there is no material that may contaminate the sample
- Withdraw approximately 3 milliliters of solution from the scintillation vial
- Attach a 0.2 micron filter and filter the solution into the auto-sample vial
- Crimp the cap onto the auto-sample vial and begin preparing the next sample

A.1.4 Running the GPC

- Place the samples into the GPC and assign the correct sample names to their corresponding sample holder numbers using the GPC analysis program
- Change the injection volume to 100 microliters (most likely already set to 10) and add any desired replicates
- Double check to make sure that the latest Polystyrene (PS) calibration reference curve is selected (ask lab manager for assistance if you cannot locate this)
- Close the auto-sampling tray on the GPC
- Press “error check” on GPC software
- If no errors are present, click on the “analyze button” and the GPC will begin to run
- Record requested information in the log book located on top of the GPC

A.1.5 Data retrieval

- After the GPC is finished running the sample, open the file in the data analysis software
- Open a blank Microsoft Excel spreadsheet
- Click on one of the sample names in the data analysis software
- Right click on the curve that appears after clicking on the sample name and click “copy data to clipboard”

- Paste the data into the MS Excel spreadsheet and type the name of the data series above the y-axis. The x-axis is time and the y-axis is the Refractive Index (mV). **Tip:** You can paste all of the data to a single spreadsheet, which will make it easier for analysis)
- Once you have retrieved the data, discard the samples

A.1.6 Data Analysis

- Analysis is performed in MS Excel
- Spreadsheet setup prior to analysis, all shown in the Figure A.1.1 below this section:
    - All x-values for the data set can be removed with the exception of the first sample. All x-values are the same, while the y-values (refractive index (mV)) will change in accordance to the sample
    - Insert a column between each of the y-values so that a baseline correction can be made if there is fluctuation in the baseline prior to the sampling. In the cell next to “Y:” put the label “y(adj)”
    - Additionally, add three rows at the top of the MS Excel spreadsheet for calculations of the large molecular sizes (LMS).
    - Above the x-axis, label the three new rows from top to bottom “LMS”, “TOTAL”, and “LMS%”

FK	FL	FM
LMS	5084.4	4996.26
TOTAL	88154.1	87925.2
LMS %	5.77%	5.68%
Chromat	EXAMPLE	0.13374
X:	Y:	y(adj)
0	0.03	-0.10374
0.00167	0.034	-0.09974
0.00333	0.041	-0.09274
0.005	0.043	-0.09074
0.00667	0.04	-0.09374
0.00833	0.034	-0.09974
0.01	0.027	-0.10674
0.01167	0.015	-0.11874
0.01333	0.007	-0.12674

Figure A.1.1. Spreadsheet setup prior to analysis

- Just above the “y(adj)” cell, calculate the average of the first 7 or 8 (engineering judgment) minutes of the chromatogram. **Tip:** Use the =AVERAGE(x:x) function in excel. Use the x-axis (minutes) to see what cells to begin and stop the analysis
- Plot all of the x values versus the y(adj) values on one figure. It will look something like the following Figure A1.2 (Note: following figure only has one chromatogram, but for multiple samples all chromatograms need to be plotted simultaneously.)

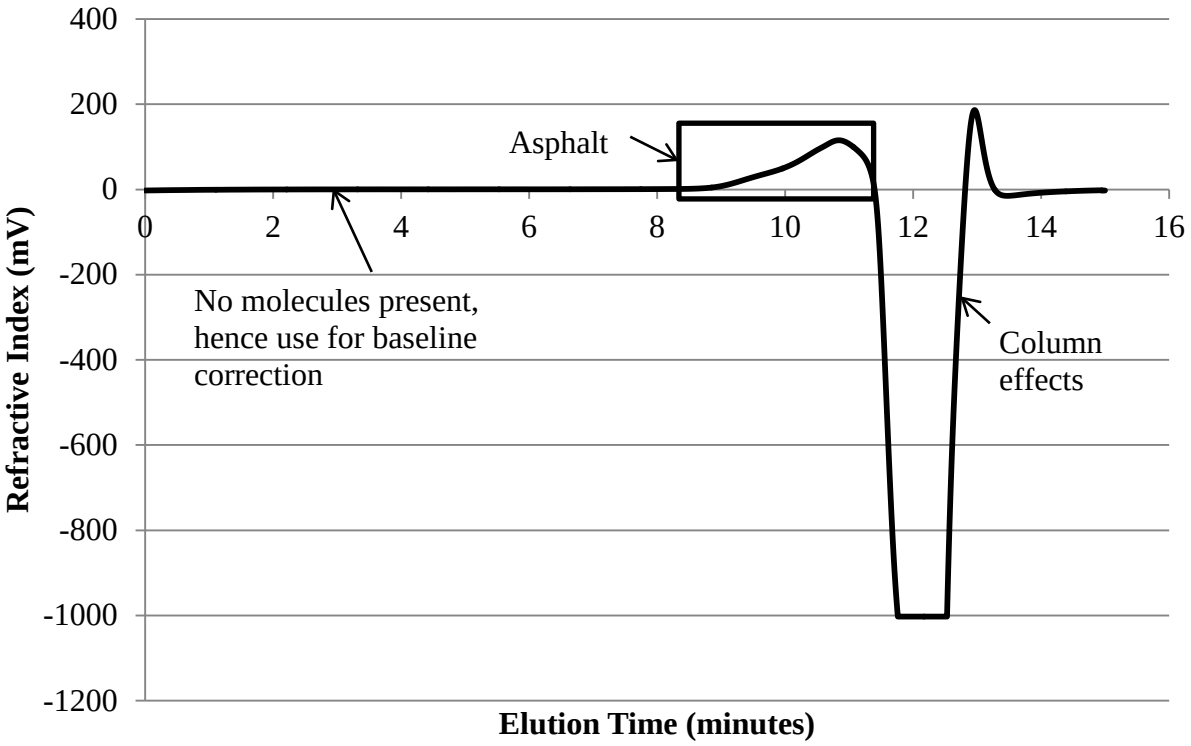

Figure A.1.2. Labeled GPC chromatogram

- Zoom into the chromatogram, as shown in the following Figure A1.3. This is where maximum and minimum limits can be set that define the chromatogram.

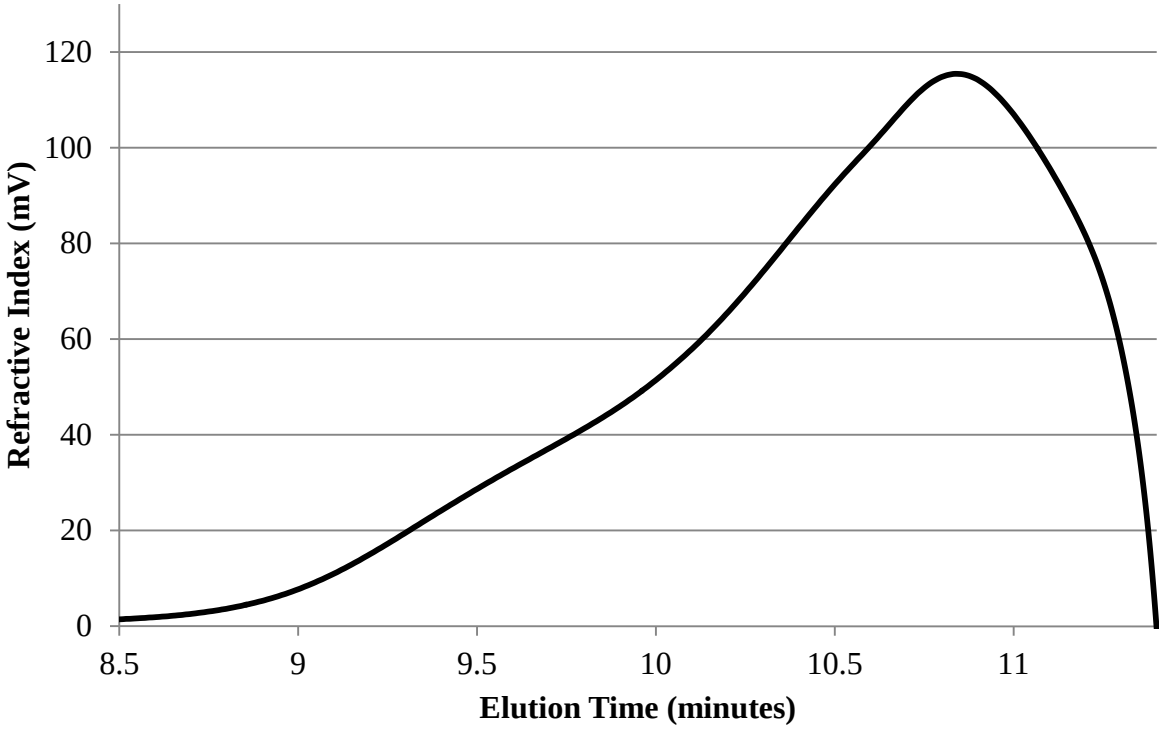

Figure A.1.3. Zoomed in GPC chromatogram

- When zooming in, set the x-axis values with a significant figure to the thousandths (0.000).
- Set the minimum limit on the x-axis (elution time) where the *first* curve begins to increase on the y-axis.
    - Reasoning: When comparing a RAP binder to a virgin binder, the RAP binder will likely have significantly more large molecules present than the virgin binder, thus it will likely also begin to show large molecules earlier in the chromatogram.
- Set the maximum limit on the x-axis (elution time) where the *first* curve falls to zero.

- Reasoning: Occasionally there will be a very slight difference between curves in terms of where the column effects begin to occur. Thus, it is best to define the maximum x-value at the point in which the first chromatogram falls to zero. If the second or third chromatogram is considered, the first chromatogram will have been integrated below zero due to the column effects.
- Note: In some cases the column effects do not allow for the chromatogram to fall all the way to zero, but actually begin to plateau somewhere before zero before climbing up to the maximum y-value. If this occurs, it is best to define the maximum x-value as the *first* chromatogram to begin to plateau. Typically, this value is estimated at the point in which the *first* curve *begins* to plateau.

- After visually setting the limits, calculate the LMS. Remember, LMS is defined as the area beneath the first 5/13 of the chromatogram. For example:
  - Minimum limit = 8.500 minutes
  - Maximum limit = 11.350 minutes
  - 11.350 – 8.500 = 2.850 minutes (This is the *total* elution time for the asphalt)
  - 2.850 x (5/13) = 1.096 minutes (This is the *LMS* of the *total* elution time)
  - 8.500 + 1.096 = 9.596 minutes
  - LMS = 8.500 → 9.596 minutes

- Look at the x-values provided by the data set and locate the cell number for 8.50 minutes, 9.60 minutes, and 11.35 minutes. For example:
    - 8.500 = cell 5106
    - 9.596 = cell 5764
    - 11.350 = cell 6816
    - **Tip:** You may also use the 11.350 and 8.500 cells (6816 and 5106) to calculate the LMS cell to make sure that it matches the 9.596. (e.g. Using 6816 and 5106 one should able to apply the 5/13 calculation previously shown and reach a number of 5764, the same cell number that marks 9.596 minutes.
- Above the y(adj) and next to LMS add the sum of all y(adj) values for the LMS. **Tip:** Do this using the =SUM() function in MS Excel. Example as follows:

LMS	=SUM(FM5106:FM5764)
TOTAL	
LMS%	
x:	y(adj)

Figure A.1.4 Example of LMS summation function

- Above the y(adj) and next to TOTAL add the sum of all y(adj) values for the total. **Tip:** Do this using the =SUM() function in MS Excel. Example as follows:

LMS	
TOTAL	=SUM(FM5106:FM6816)
LMS%	
x:	y(adj)

Figure A.1.5 Example of total summation function

- Above the y(adj) calculate the LMS% by dividing the LMS cell by the TOTAL cell. Then format the cell to be in *percentage* not number. Example:

LMS	
TOTAL	
LMS%	=LMS cell / TOTAL cell
x:	y(adj)

Figure A.1.6 Example of LMS% division function

- Do this for *all* data and then compare the LMS% for each.

A.2.0 Procedure for Fourier Transform Infrared Spectroscopy and Data Analysis

A.2.1 Important Notes of Consideration

This procedure was developed using the Nicolet 6700 Spectrometer. Before running test, make sure that proper training has taken place. Films are created for testing by drop casting asphalt solution onto potassium bromide (KBr) salt plates. While this technique is not difficult, it is vastly improved through experience.

When working with solvents for sample preparation, in this case Toluene, make sure to be familiarized with the Material Safety Data Sheet (MSDS) and to have all proper protective equipment.

A.2.2 Sample Preparation

- Use toluene solvent to clean the potassium bromide (KBr) salt plates used for sampling
- Approximately 2 mL (dependent on need) of toluene was added to the asphalt mixture in a 20 mL scintillation vial. The asphalt was typically already in this vial as a product of the recovery process from the staged extraction method.
- The vial, with toluene, was mixed on a rotating vial shaker for at least one minute until all the binder was dissolved in the solvent.
    - **Tip:** At this stage in the process, the effort is to simply make the asphalt binder flow at a high viscosity, not to cause it to run like a Newtonian fluid (i.e. water). A higher viscosity will allow for solvent to evaporate from the asphalt at a higher rate during the drop casting process, described herein, and will generally yield better films.
- After dissolving the binder, use a new disposable glass pipette to drop 2-4 drops (depending on viscosity). Take the KBr salt plate and slowly rotate it in the air, moving the droplets of asphalt solution around the plate. This process both

increases the rate of evaporation as well as allows for control of asphalt film thickness

  - **Tip**: Experience shows that if a film is too thick or too thin it will not yield a good IR spectra. The goal is to create a film that is amber in color.

- Once the sample is dry, place it in the vacuum oven for at least 12 hours at 100°C. Make sure that the vacuum is applied so that oxidation has not occurred. This is done to ensure that all of the toluene solvent has evaporated from the sample and will not affect the IR spectra.

A.2.3 Operating the FTIR

- Turn on the PC connected to the FTIR
- Once the PC has turned on, open the OMNIC software that is used for FTIR data acquisition and analysis
- Turn on the FTIR and allow it to warm up for a minimum of 15 minutes
- Place the KBr salt plate into the sample holder
- Select “Collect” → “Experimental setup”
  - Choose the number intended number of scans (traditionally 64 scans used, in some cases more)
  - Select “collect background after sample” option
  - Close the dialogue box
- Click “Collect” → “Collect Sample”

- After the completion of the 64 scans, the user will be prompted to remove the sample and begin collecting the background. Remove the sample, then click “OK”
- After the background is complete the user will be prompted to give the sample a name and press “OK”

A.2.4 Spectral Analysis

- There are multiple methods of analysis that can be considered. The one discussed as follows is using the “peak area” method.
- Consider the area of focus for the Carbonyl (C=O) at 1695 cm-1 and Saturated C-C stretch at 1455 cm-1 for aging, as indicated in the following figure. Note the growth of the carbonyl between Figure A2.1 and Figure A2.2.
    - **Tip:** It is recommended to have a maximum absorbance between 0.3 and 0.9.
    - **Tip:** When comparing multiple spectra, use the Match Scale button located near the top of the menu to change the maximum peak y-value to match that of the selected spectra. The maximum peak should be Saturated C-C.

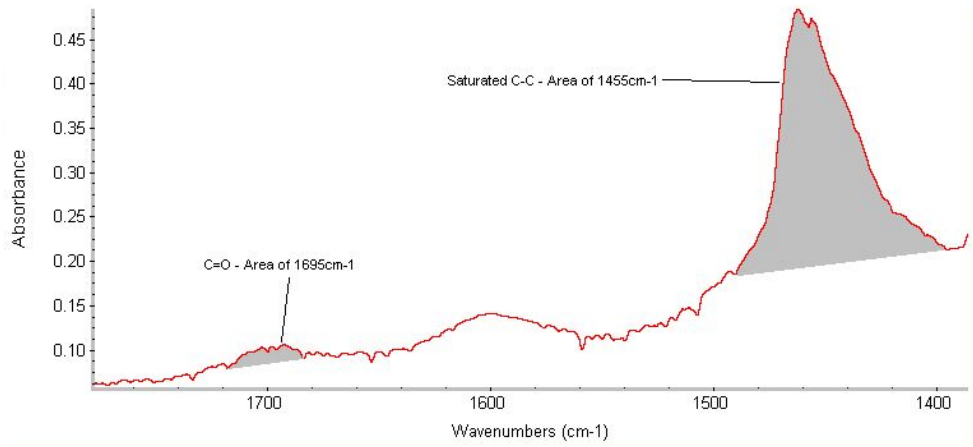

Figure A2.1 Carbonyl band area and saturated C-C band area for unaged binder

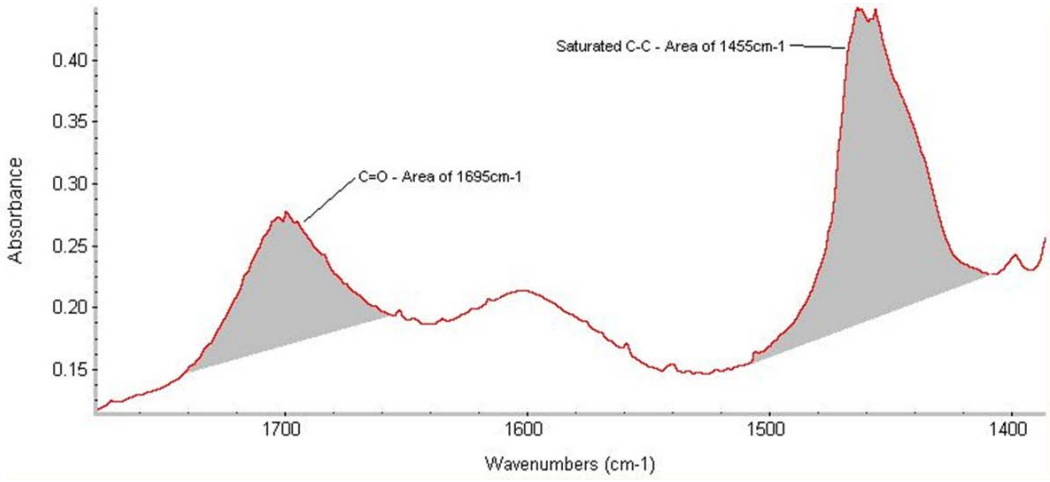

Figure A2.2 Carbonyl band area and saturated C-C band area for aged binder

- Previous studies indicated that the best peak area ranges for the Carbonyl (C=O) at 1695 cm^{-1} and Saturated C-C stretch at 1455 cm^{-1} are from 1672-1718 cm^{-1} for the carbonyl and 1435-1473 cm^{-1} for the saturated C-C.
    - When taking the area beneath the peak, an uncorrected area will be provided. Record this number (MS Excel recommended).

- Note: The area values provided are negotiable based on engineering/scientific judgment and experience

- Using the calculated area beneath the peak calculate the aging index (AI) also interchangeably called the Carbonyl Index (CI) using the following equation:

$$Aging\ Index\ (AI) = \frac{Area\ of\ the\ Carbonyl\ peak\ at\ 1695\ cm^{-1}}{Area\ of\ the\ C{-}C\ streth\ peak\ at\ 1455\ cm^{-1}} \quad \text{(A.2.1)}$$

- Save all data before closing program and turning of FTIR.

VITA

Benjamin Frank Bowers was born in 1987 in Charlotte, North Carolina. He began his academic studies at the University of North Carolina at Charlotte in Charlotte, North Carolina in 2005 where he attained his Bachelors of Science in Civil and Environmental Engineering in 2009. During his final semester as an undergraduate student he began pursuing his Masters of Science in Civil Engineering at the University of North Carolina at Charlotte as an early admissions graduate student. He completed a thesis entitled "Effect of Calcium Chloride on Cement Stabilization of Soils" under the direction of his advisor, Dr. John L. Daniels. He attained his Masters of Science in Civil Engineering in August of 2010. Mr. Bowers began his studies at the University of Tennessee, Knoxville as a Ph.D. student studying under the direction of Dr. Baoshan Huang in August of 2010. He will attain his Doctorate of Philosophy in Civil Engineering with a focus in Geotechnical and Materials Engineering in December of 2013. During his time at the University of Tennessee, Knoxville he extended his research area into that of recycled materials in asphalt pavement and chemical testing techniques.